[illegible] 17 1925

VOLUME [illegible] SECOND SERIES NUMBER 3

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

THE

AMERICAN PHYSICAL SOCIETY

BOARD OF EDITORS

Managing Editor: George [illegible], Cornell, New York;
A. H. Compton, E. H. Kennard, [illegible] Page; H. D. Babcock, W. G. Cady,
John T. Tate; K. K. Darrow, R. C. Kemble, F. L. Mosher

SEPTEMBER, 1925

Directed Quanta of Scattered X-rays – – – Arthur H. Compton and Alfred W. Simon 289
Wave-lengths of Scattered X-rays – – – – Samuel K. Allison and William Duane 309
Series Spectra of Two-valence-electron Atoms: Boron and Carbon
– – – – – – – – – – – – I. S. Bowen and R. A. Millikan 310
The Spectrum of Silicon Nitride – – – – – – – – – Robert S. Mulliken 319
Ionization of HCl by Electrons – – – – – – E. F. Farker and O. S. Duffendack 339
Secondary Electron Emission from Iron, Nickel and Molybdenum – Robert L. Peters 346
Negative Ion Emission from Oxide Coated Filaments – – – – – Henry A. Barton 360
Persistence of the Radiation Excited in Mercury Vapor – – – – – Lucy J. Hayner 364
Duration of Fluorescence of Mercury Vapor – – – – – – – R. N. Ghosh 378
Optical Constants of Magnesium and Zinc [illegible] – – – – – – M. E. Garbee 389
Orientations of Crystals in Electrodeposited Metals – – – – Richard M. Bozorth 399
Binaural Beats – – – – – – – – – – – – – – – C. E. Lane 421
Book Reviews – 429

PUBLISHED BY THE AMERICAN PHYSICAL SOCIETY
[illegible], N. Y.

THE AMERICAN PHYSICAL SOCIETY

OFFICERS OF THE SOCIETY

President:	D. C. Miller	Case School of Applied Science, Cleveland, Ohio
Vice-President:	K. T. Compton	Princeton University, Princeton, N. J.
Secretary:	H. W. Webb	Columbia University, New York City
Treasurer:	G. B. Pegram	Columbia University, New York City
Editor:	G. S. Fulcher	Corning, N. Y.
Local Secretary for the Pacific Coast:	D. L. Webster	Stanford University, Calif.

THE PHYSICAL REVIEW

Published monthly — Two volumes annually

First series. From July 1, 1893 to January 1, 1913, the Review was conducted by Edward L. Nichols, Ernest Merritt and Frederick Bedell, with the financial support of Cornell University. The first four volumes were issued annually; subsequent volumes semi-annually; thirty-five volumes in all.

Second series. On January 1, 1913, the Review was transferred to the American Physical Society as announced on the first page of the new series which was then begun. Since then it has been conducted by a Board of Editors elected by the Society. Semi-annual volumes begin in January and July.

Contributors are referred to page 2 of the advertisements for further information.

Annual Subscription, throughout the Postal Union, $7.00 in advance.

Single Copies, $.75.

General Index, 1893-1920, $4.00, in advance.

Back Volumes, $1.50 per volume; **Back Numbers,** $.75 per copy. Postage is free if remittance accompanies order; otherwise postage is extra. No bound volumes can be supplied. The Review offers to purchase a limited number of First Series, Vol. 1, No. 1 (at $1.50 each); Second Series, Vol. 7, No. 1, January 1916; Vol. 7, March 1916 and Vol. 9, No. 2, February 1917 (at $1.50 each); Vol. 19, No. 1, January 1922 (at $.75 each).

Advertisements. Rates will be supplied by the Editor on request. Copy for each number must be received at Corning before the 1st of the preceding month; old copy is used until new copy is received. Send electrotypes direct to the printers, George Banta Publishing Co., Menasha, Wisconsin.

Discount of ten percent is allowed subscription agencies and members of the American Physical Society.

Complaints of failure to receive the Review, in the case of members of the Physical Society, should be addressed to the Treasurer; otherwise, to the Review, Corning, N. Y. *New copies will be sent free only if complaint is received within three months of date of issue.*

Correspondence should be addressed to the Physical Review, Corning, N. Y.

Entered at the postoffice at Menasha, Wis., as second class matter.
Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized September 6, 1923

Second Series *September, 1925* *Vol. 26, No. 3*

THE

PHYSICAL REVIEW

DIRECTED QUANTA OF SCATTERED X-RAYS

By Arthur H. Compton and Alfred W. Simon[1]

Abstract

Relation between the direction of a recoil electron and that of the scattered x-ray quantum.—It has been shown by cloud expansion experiments previously described, that for each recoil electron produced, an average of one quantum of x-ray energy is scattered by the air in the chamber. If the quantum of scattered x-rays produces a β-ray in the chamber, then a line drawn from the beginning of the recoil track to the beginning of the β-track gives the direction of the ray after scattering. Using a chamber 18 cm in diam. and 4 cm deep traversed by a carefully shielded narrow beam of homogeneous x-rays, with exploded tungsten wires as sources of light, nearly 1300 stereoscopic cloud expansion photographs were taken. Of the last 850 plates, 38 show both recoil tracks and β-tracks. The angles projected on the plane of the photographs were measured and it was found that in 18 cases, the direction of scattering is within 20° of that to be expected if the x-ray is scattered as a quantum so that energy and momentum are conserved during the interaction between the radiation and the recoil electron. This number 18 is four times the number which would have been observed if the energy of the scattered x-rays proceeded in spreading waves, that is if the direction of production of a β-ray was unrelated to the direction of the recoil track. The chance that this agreement with theory is accidental is about 1/250. The other 20 β-rays are ascribed to stray x-rays and to radioactivity. This evidence seems a direct and conclusive proof that at least a large proportion of the scattered x-rays proceed in directed quanta of radiant energy.

AN increasingly large group of phenomena has recently been investigated which finds its simplest interpretation on the hypothesis of radiation quanta, proposed by Einstein to account for heat radiation and the photo-electric effect.[2] It has not been possible, however, to show that any of these phenomena necessarily demand this hypothesis for its explanation. Thus, for example, the photo-electric effect is not inconsistent with the view that the light energy proceeds from its source in expanding waves, if we postulate the existence within atoms of a

[1] National Research Fellow.

[2] An interesting summary of this work has been presented by K. K. Darrow in the Bell Technical Journal **4**, 280 (1925).

mechanism for storing energy until a quantum has been received. It is true that no such mechanism is known; but until our knowledge of atomic structure is increased it would be premature to assert that such a storing mechanism cannot exist. The change of wave-length of x-rays when scattered and the existence of recoil electrons associated with scattered x-rays, it is true, appear to be inconsistent with the assumption that x-rays proceed in spreading waves if we retain the principle of the conservation of momentum.[3] Bohr, Kramers and Slater,[4] however, have shown that both these phenomena and the photo-electric effect may be reconciled with the view that radiation proceeds in spherical waves if the conservation of energy and momentum are interpreted as statistical principles.[5]

A study of the scattering of individual x-ray quanta and of the recoil electrons associated with them makes possible, however, what seems to be a crucial test between the two views of the nature of scattered x-rays.[6] On the idea of radiation quanta, each scattered quantum is deflected through some definite angle ϕ from its incident direction, and the electron which deflects the quantum recoils at an angle θ given by the relation[7]

$$\tan \tfrac{1}{2}\phi = -1/[(1+\alpha)\tan \theta], \qquad (1)$$

where $\alpha = h/mc\lambda$. Thus a particular scattered quantum can produce an effect only in the direction determined at the moment it is scattered and predictable from the direction in which the recoiling electron proceeds. If, however, the scattered x-rays consist of spherical waves, they may produce effects in any direction whatever, and there should consequently be no correlation between the direction in which recoil electrons proceed and the directions in which the effects of the scattered x-rays are observed

To make the test it is, of course, necessary to observe the individual recoil electrons and to detect the individual scattered quanta.[8] This we have done by means of a Wilson cloud expansion apparatus, in the manner shown diagrammatically in Fig. 1. In a recent statistical study,

[3] Cf A. H. Compton, Jour. Franklin Inst. **198**, 71 (1924).

[4] N. Bohr, H. A. Kramers and J. C. Slater, Phil. Mag. **47**, 785 (1924).

[5] It seems that there still remains a difficulty in accounting on this view for the intensity of scattered x-rays. See Y. H. Woo, Phys. Rev. **25**, 444 (1925).

[6] The possibility of such a test was suggested by W. F. G. Swann in conversation with Bohr and one of us in November 1923.

[7] Cf P. Deybe, Phys. Zeits. (Apr. 15, 1923); A. H. Compton and J. C. Hubbard, Phys. Rev. **23**, 444 (1924).

[8] A preliminary account of this work has been given in Proc. Nat. Acad. Sci. **11**, 303 (June, 1925).

we have found[9] that on the average there is produced about one recoil electron for each quantum of scattered x-rays. Each recoil electron produces a visible track, and occasionally a secondary track is produced by the scattered x-ray. When but one recoil electron appears on the same plate with the track due to the scattered rays, it is possible to tell at once whether the angles satisfy Eq. (1). If the photographs and the measurements can be made with sufficient definiteness, the experiment should thus give an unequivocal answer to the question whether the energy of a scattered x-ray quantum is distributed over a wide solid angle or proceeds in a definite direction.[10]

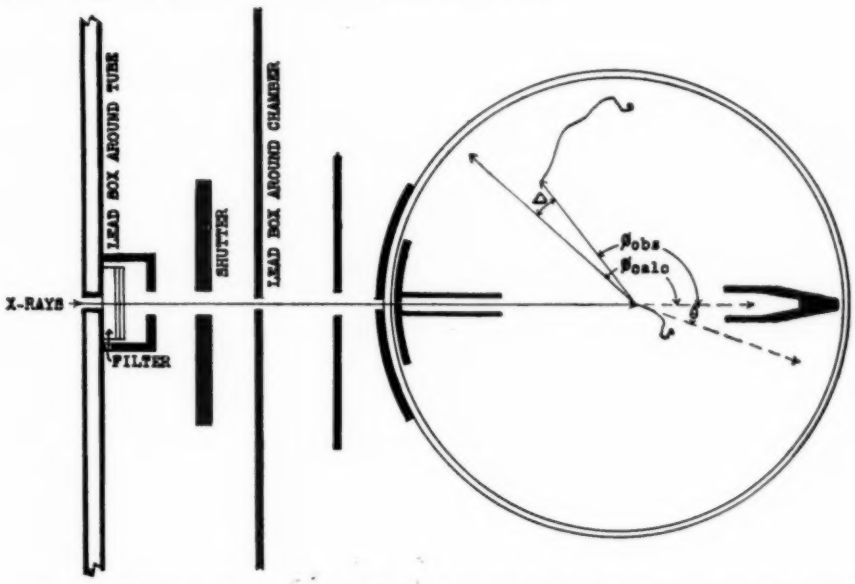


Fig. 1. Diagram of apparatus. On the hypothesis of radiation quanta, if a recoil electron is ejected at an angle θ, the scattered quantum must proceed in a definite direction ϕ_{calc}. In support of this view, many secondary β-ray tracks are found at angles ϕ_{obs} for which Δ is small.

Experimental procedure. In the final experiments we used a high voltage Coolidge x-ray tube excited by an unrectified alternating cur-

[9] A. H. Compton and A. W. Simon, Phys. Rev. **25,** 306 (1925).

[10] W. Bothe and H. Geiger have proposed (Zeits. f. Phys. **26,** 44, 1924) and carried out (Naturwissenschaften **20,** 440, May 15, 1925) a rather similar test. Using two point counters, one to receive the scattered x-rays and the other to receive the recoil electrons, they have found that many of the recoil electrons occur simultaneously with β-rays excited by the scattered x-rays. While such an experiment affords less definite evidence than does the present one regarding the directive nature of the scattered x-rays, it is equally incompatible with Bohr, Kramers and Slater's statistical view of the production of photo and recoil electrons.

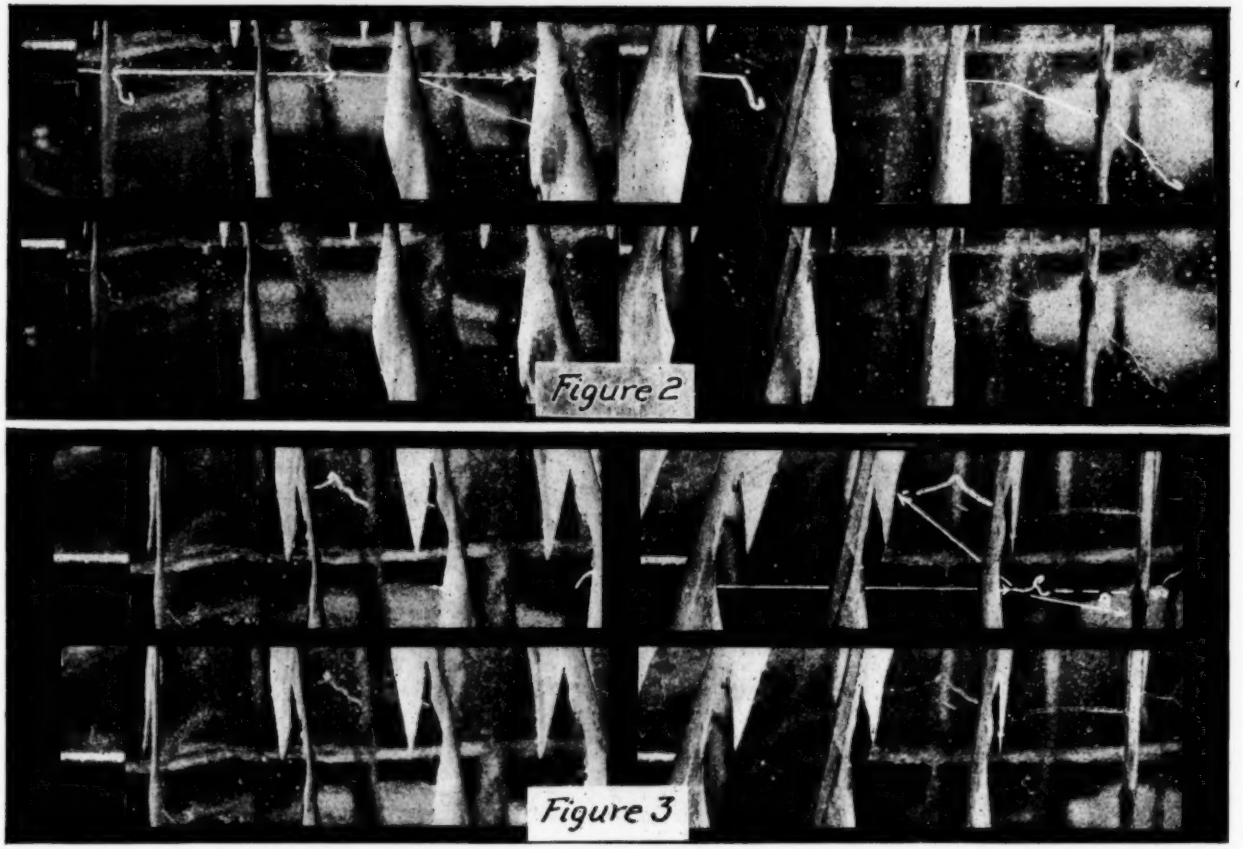


Fig. 2. A square hit. Plate 597. 1 recoil track, 1 secondary. $\theta = -2°$; $\phi_{calc} = +175°$; $\phi_{obs} = +177°$; $\Delta = 2°$.
Fig. 3. Plate 560. 2 recoil tracks, 1 secondary. $\theta = -25°$; $\phi_{calc} = +120°$; $\phi_{obs} = +120°$, $\Delta = 0°$. Recoil track (2) lies in wrong plane to be associated with secondary track.

rent at 140 peak kilovolts. Potentials as high as 250 kv were tried, but the resulting tracks of the recoil electrons were inconveniently long, and it was difficult to shield the expansion chamber adequately from the very penetrating direct rays. The x-rays were rendered approximately homogeneous by filtering through 6 mm of brass and about 2 mm each of copper and aluminium. Effects of stray x-rays were reduced to a minimum by surrounding the x-ray tube by a box of 9 mm lead, surrounding the expansion chamber with a box of 3 mm lead, and interposing suitable additional lead screens as shown diagrammatically in Fig. 1. The illumination was produced by exploding tungsten wires,[11] 0.1 mm in diameter and 14 cm long, by condenser discharges. The condenser, of about 0.1 microfarad capacity, was charged to about 70 kv by means of a separate transformer and "kenotron" thermionic rectifier. It was found necessary to surround this rectifier also with a box of 3 mm lead in order to avoid stray x-rays. The light entered the expansion chamber horizontally, at right angles to the primary beam, and the photographs were taken through the top of the expansion chamber in such a manner that the light was scattered by the water droplets at an angle of about 40°. We used an Ontoscope stereoscopic camera of 5.5 cm focal length, with the lenses stopped down to $f/8$. This gave ample exposure and a focus so deep that a β-ray track in any part of the chamber could be identified. Both the camera and the illuminating spark were enclosed within the lead box surrounding the expansion chamber.

In order to increase the probability that the scattered x-rays would produce β-ray tracks, a comparatively large chamber, about 18 cm in diameter by 4 cm high, was used. Diaphrams of thin lead foil were also suspended inside the chamber (see Figs. 2 to 5), so that the scattered x-rays might make themselves evident by ejecting photo-electrons. We allowed the primary rays to enter through a collimating lead tube, and absorbed them in a hollow lead cone. This eliminated almost completely the effect due to the scattering of the primary rays by the glass walls. When the expansion occurred, however, a slight blast of air proceded from each of these lead tubes, and distorted the tracks for a distance of about 2 cm from the collimator and about 1 cm from the absorbing cone. It was accordingly possible to make accurate measure-

[11] The illumination obtained using the tungsten wires was roughly 10 times as brilliant photographically as that from a mercury spark at atmospheric pressure, using the same electrical energy.

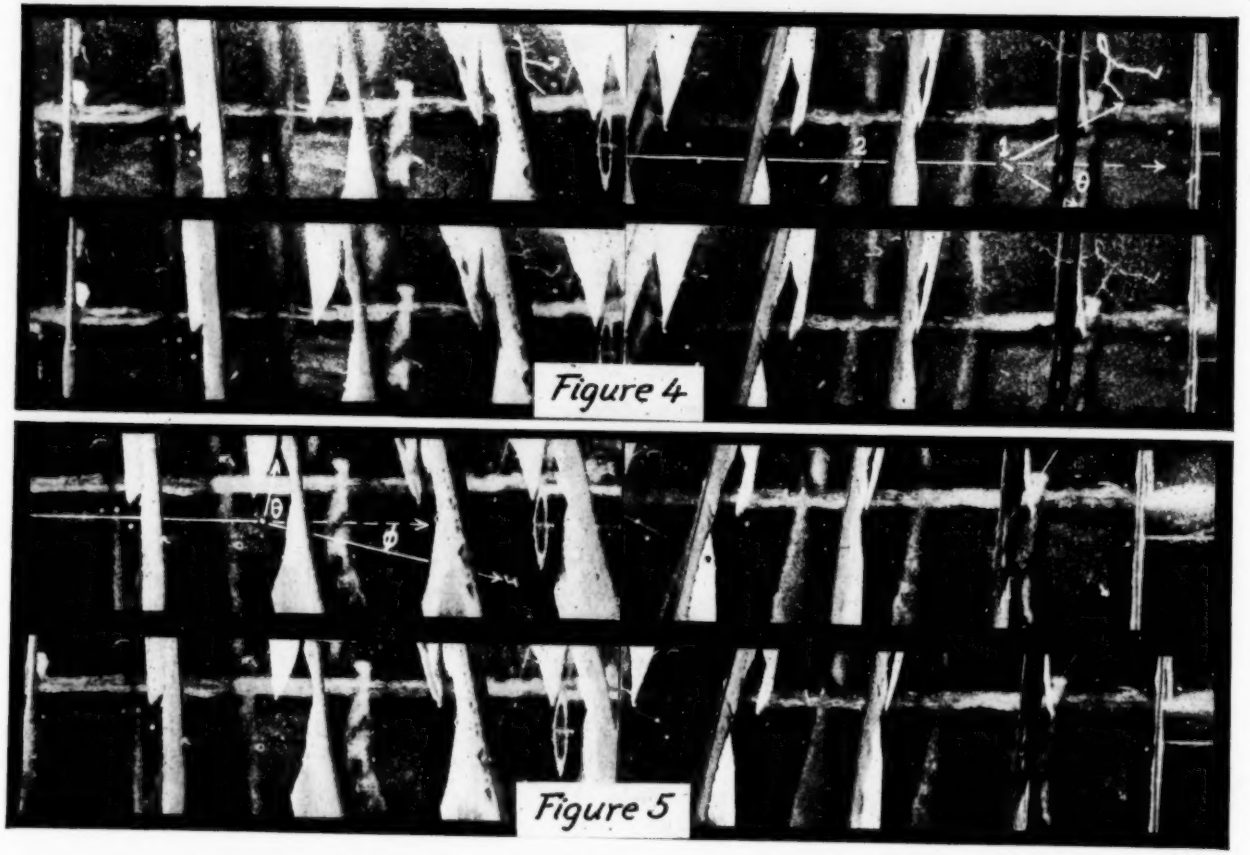


Fig. 4. Plate 1018. 2 recoil tracks, 1 secondary. $\theta = -55°$; $\phi_{calc} = +59°$, $\phi_{obs} = +50$; $\Delta = 9°$.
Fig. 5. A glancing blow. Plate 725. 1 recoil (sphere) track, 1 secondary. $\theta = \pm 85°$ as estimated from length of track; $\phi_{calc} = \pm 8°$, $\phi_{obs} = -22°$; $\Delta = 14°$ or $30°$.

ments only on those recoil electrons which were ejected from a column of air about 4 cm long near the middle of the expansion chamber.

An examination of the photographs indicates that there was 1 β-ray produced by x-rays scattered from this air column for about every 50 recoil electrons originating in this region, in satisfactory accord with a rough calculation based on the absorption coefficients of the x-rays and β-rays. There were in addition a considerable number of stray β-rays, due in part to stray x-rays and to radioactivity, as was shown by preventing the direct rays from entering the chamber, and probably in part also to the incompletely shielded scattered rays from the walls of the expansion chamber. The presence of these stray rays does not, however, present a serious difficulty in interpreting the photographs, since obviously there can be no correlation between their positions and the directions of ejection of the recoil electrons. Thus the effect of the scattered rays is a definite one superposed upon a random effect due to the stray β-rays.

The photographs. In making the preliminary adjustments and for auxiliary experiments we took about 140 photographs. The pictures which were useful in the final test were divided into three series. In the first series there were 302 plates. The second series of 338 plates and the third series of 511 plates were taken under improved conditions of x-ray shielding, thus reducing the number of stray β-ray tracks. There appear on the average two or three recoil tracks in each picture.

Typical photographs in which the secondary tracks appear are shown stereoscopically ($\times 1.3$) in Figs. 2, 3, 4 and 5. In each case a retouched photograph with arrows marking the direction of the primary, recoil and scattered rays is placed above the untouched photograph. Unfortunately there appear on these plates also other marks due to water drops, pieces of lint, bubbles in the glass, etc. While these mar the beauty of the photographs, they do not impair their value, since such marks can always be identified by comparing successive plates.

Analysis of the photographs. An angular scale was placed on top of the expansion chamber and photographed with the camera raised half the height of the chamber. A transparency print of the resulting photograph was superposed on the negative of the tracks to be measured. By this means we measured the angles approximately as they would be projected on the plane of the top of the cylindrical chamber. We did not find it possible by means of the stereoscopic effect to make reliable estimates of angles in a plane including the line of sight. The

measurements were made on the original negatives, using a stereoscope with lenses of the same focal length as those of the camera.

When only one recoil electron and one secondary electron appeared on a photograph, the procedure was to record first the angle θ at which the track of the recoil electron begins. The end representing the origin was rarely doubtful, since these tracks started within a narrow cylinder of air only about 1 mm in diameter. The angle between the incident ray and the line joining the origin of the recoil track and the origin of the secondary track was noted (when the origin of the secondary track

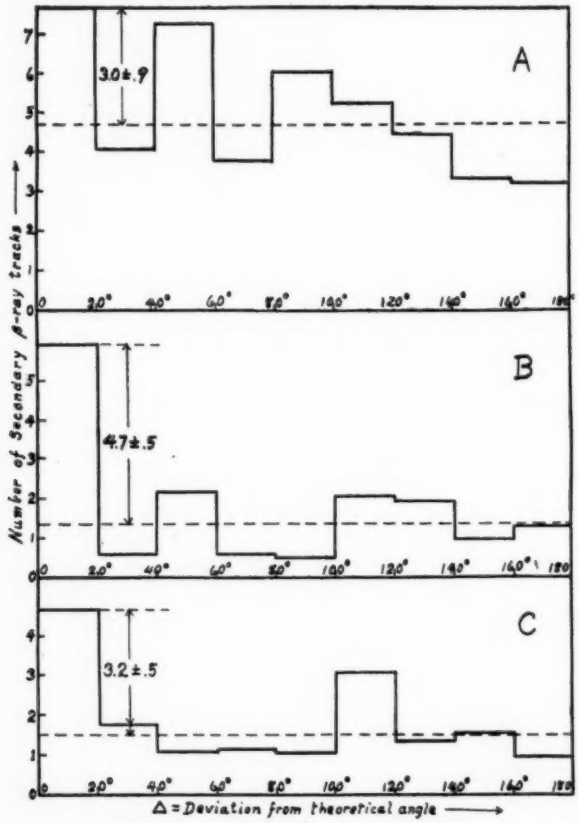


Fig. 6. The weighted number of secondary tracks at different angles Δ from the theoretical position. The exceptionally large number between 0 and 20° indicates that many secondary tracks are due to rays scattered as directed quanta. Curve A: Some stray x-rays present. Curves B and C: Most of stray rays eliminated by lead screens.

could not be identified the measurement was made to a point midway between its two ends). The difference between this angle and the angle ϕ calculated from θ by equation (1) was called Δ, and this value of Δ

was assigned a weight of unity. When a number n of recoil tracks appeared on the same plate with a secondary track, the value of Δ was thus determined for each recoil track separately, and assigned a weight $1/n$. Following this procedure there are values of Δ which are distributed approximately at random between 0 and 180° due to the $n-1$ recoil electrons which are not associated with the secondary track. This is in addition to the random values of Δ resulting from the presence of occasional stray tracks. We discarded the plates on which more than 3 recoil tracks appeared.

The results of this analysis are summarized in Figs. 6 and 7. Figure 6A shows the results for the first 302 plates, in which there appeared about 1 stray track for every 4 photographs. As will be seen, this was almost enough to hide the presence of the comparatively rare tracks due to scattered rays, which nevertheless show themselves by the exceptional concentration of Δ values between 0 and 20°. Figs. 6B and

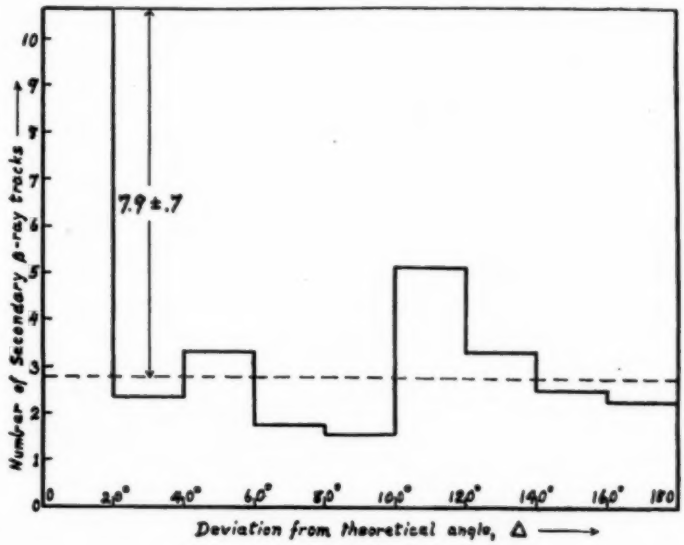


Fig. 7. Sum of curves 6B and 6C.

6C represent respectively the second and third series of plates, in which, by improving the lead shielding, the total number of secondary tracks was reduced to about 1 for every 20 plates. It will be seen that the result of this is to lower the general level of the random Δ values and thus to exhibit much more prominently the concentration of these values at small angles. It is just such a concentration which is to be expected if Eq. (1) holds, that is if individual quanta are scattered in definite

directions from individual electrons. In Fig. 7 we have collected the results of the second and third series of plates. This figure shows the distribution of 38 secondary β-rays observed on these plates, 18 of which originate within 20° of the position anticipated from one of the recoil tracks present. The number 18 is about 4 times as many as would be expected if the distribution of the secondary tracks were a matter of chance. An idea of the degree of definiteness of the results can be obtained by calculating the probable variation from the mean of each of the 8 values between 20° and 180° by the usual formula, $\pm.67\sqrt{\Sigma\delta^2/(n-1)}$, where δ is the deviation of each value from the mean, and n is the number (8) of values. Thus we find that the number of pairs occurring with values of Δ less than 20° is greater than the mean value for the other angles by 7.9 ± 0.7. The probability that so great an accidental deviation would occur in the positive direction is accordingly $(1/2)\times(.7^2/7.9^2)=1/250$. It is thus highly improbable that so many pairs of tracks should as a matter of chance have been found to fit Eq. (1) satisfactorily.

Two other possibilities remain, (1) that the observed coincidences are the result of an unconscious tendency to estimate the angles falsely, making consistently favorable errors in measurement, and (2) that the agreement with Eq. (1) is real. Regarding the first possibility, we may note that using our methods of measurement it was hardly possible to make an error in determining the angle of ejection of the recoil electron of more than 10° nor in the angle at which the secondary electron appeared of more than 5°. It will be seen that errors of this magnitude could not alter the general form of the curve. The evidence therefore seems unescapable that Eq. (1) describes to a close approximation the angles at which many of the secondary electrons appear.

The question arises, does the presence in Fig. 7 of the considerable number of values of Δ greater than 20° indicate the existence of scattered rays which do not obey the quantum law? It can be shown that about half of these random values of Δ are to be expected merely from the fact that in most of the cases where Eq. (1) describes accurately the relation between the position of the secondary electron and the direction of motion of one recoil electron, there are one or two other recoil electrons which are in no way associated with the secondary β-ray. We are unable to assign definitely the origin of the remaining half of the random Δ values. Undoubtedly some are due to stray x-rays which could not be completely eliminated and some are probably due to β-rays of radioactive origin. Our experiments cannot therefore be taken to

afford any evidence for the production of β-rays by scattered x-rays which do not conform to the quantum rule described by Eq. (1).

It is our conclusion, therefore, that at least a large part of the scattered x-rays under investigation produce β-rays at an angle connected by equation (1) with the angle of ejection of an associated recoil electron.

Since the only known effect of x-rays is the production of β-rays, and since the meaning of energy is the ability to produce an effect, our result means that there is scattered x-ray energy associated with each of these recoil electrons sufficient to produce a β-ray and proceeding in a direction determined at the moment of ejection of the recoil electron. In other words, at least a large part of the *scattered x-rays proceed in directed quanta of radiant energy.*

Since other experiments have shown that these scattered x-rays can be diffracted by crystals, and are thus subject to the usual laws of interference, there is no reason to suppose that other forms of radiant energy possess an essentially different structure. It thus becomes highly probable that all electromagnetic radiation is constituted of discrete quanta proceeding in definite directions. It is not impossible to express this result in terms of waves if we suppose that a wave train possesing a single quantum of energy can produce an effect only in a certain predetermined direction.

These results do not appear to be reconcilable with the view of the statistical production of recoil and photo-electrons proposed by Bohr, Kramers and Slater. They are, on the other hand, in direct support of the view that *energy and momentum are conserved during the interaction between radiation and individual electrons.*

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO.
June 23, 1925.

EXPERIMENTS ON THE WAVE-LENGTHS OF SCATTERED X-RAYS

By Samuel K. Allison[1] and William Duane

Abstract

Intensity distribution of scattered x-rays as a function of wave-length.—(1) *Molybdenum rays.* Specially built tubes enabled the radiators to be placed only 1.6 cm from the target, so that reliable measurements were obtained from small radiators. An ionization spectrometer (methyl iodide) with a calcite crystal was used. For Li and Al, curves are given for various scattering angles. The results are similar to those obtained by previous observers for carbon, the shift of the maximum intensity of the modified band agreeing with the theory of A. H. Compton. Simultaneous irradiation by two x-ray tubes permitted scatterers to be employed that were small enough to allow a fairly accurate estimate of the *width of the modified band.* This width (for lithium) was thus found to be greater than that permitted by Compton's equation. The curves obtained show that the intensity of the unshifted line relative to the general radiation is less in the scattered spectrum than when obtained direct from the target of the tube. Less detailed experiments with Be, C, Na, NaCl, Mg and S are in agreement with the theory as far as shift is concerned and show that the relative intensity of the modified band decreases as atomic number increases. (2) *Tungsten rays.* In this case the radiator could not be placed nearer than 10 cm, so less reliable results were obtained. However the shifts are in general agreement with theory.

PRELIMINARY reports of these experiments have appeared elsewhere.[2,3] The experiments were performed with one of the ionization spectrometers in this laboratory which has been previously described.[4,5] The preliminary reports mentioned the use of special water-cooled x-ray tubes, similar to those first designed by A. H. Compton,[6] and of the multiple slits devised by Soller.[7] The water-cooled molybdenum targets in the special x-ray tubes were of the type furnished by the General Electric Company in the apparatus manufactured for experiments on x-ray diffraction. These targets were sealed into long, narrow, glass tubes constricted and made thin-walled in a region near the focal spot. With such tubes the scattering substance should be brought within 1.6 cm of the center of the focal spot. No great difficulty was experienced in evacuating these tubes

[1] National Research Fellow.
[2] Allison and Duane, Proc. Nat. Acad. Sci. **11**, 25 (1925).
[3] Allison and Duane, Phys. Rev. **25**, 235 (1925).
[4] Allison and Duane, J. Opt. Soc. Amer. and Rev. Sci. Inst. **8**, 681 (1924).
[5] J. C. Hudson, ibid., **9**, 259 (1924).
[6] A. H. Compton, Phys. Rev. **22**, 409 (1923).
[7] Soller, Phys. Rev. **23**, 272 (1924).

so that they could be sealed off and run at 50 kv and 20 milliamp. from the high potential storage battery.

The multiple slits were constructed with 15 vanes of spring steel, 1 cm wide by 50 cm long, and .015 cm thick. These vanes were held between brass plates in which parallel grooves had been cut. Thus 14 parallel slits 50 cm long were produced, each slit .07 cm broad and 1 cm high. The calculated angular width of the beam from the slits was therefore 9.6 minutes of arc. The width of the unresolved Mo $K\alpha$ doublet should then be 12.1 minutes of arc in the first order. The observed width agreed well with this calculation.

The composite beam from these slits was 1 cm wide and necessitated therefore a crystal face 8.7 cm long in order to reflect the whole beam at an angle of incidence of 6°30′. (The critical angle of reflection of the Mo $K\alpha_1$ line is 6°43′.) An old face on a calcite crystal 9.2 cm long was finally adopted. This face was shown not to give spurious reflections by examining the Mo $K\alpha$ lines direct from the target of the tube.

In the course of the work a set of curves was obtained which showed the change of wave-length of the modified radiation with scattering angle in the case of the scattering of molybdenum rays by lithium. Later these experiments were repeated with the beam defined only by two single slits and reflected from one of the crystals previously used for wave-length determinations in this laboratory. The curves obtained in this way confirmed completely the results from the multiple slits and large crystal, and also showed that the increase in intensity obtained by the use of multiple slits is really surprisingly small.

The gain in intensity due to the narrow x-ray tubes enabled us to use small radiators, or, what amounts to the same thing, to select for examination radiation from a portion of the scatterer in which the range of scattering angle is small. The importance of this has been previously considered,[2] and will be illustrated later.

In examining the scattering of molybdenum rays we have made more or less isolated experiments using scatterers of Be, C, Na, NaCl, Mg, and S. We have made more extensive studies of the scattering by Al and Li. The results confirm those of other experimenters who have published curves or photographs representing the scattering of Mo x-rays in a similar manner.[8–12] They show that in addition to scat-

[8] A. H. Compton, Phys. Rev. **21**, 483 (1923) et seq.
[9] P. A. Ross, Proc. Nat. Acad. Sci. **9**, 246 (1923) et seq.
[10] Compton and Woo, Proc. Nat. Acad. Sci. **10**, 271 (1924).
[11] J. A. Becker, Proc. Nat. Acad. Sci. **10**, 342 (1924).
[12] Kallman and Mark, Naturwiss. **14**, 299 (1925).

tered radiation having the same wave-length as the primary, as demanded by the classical theory of scattering, there is, at least for the light elements, a large portion of the scattered radiation which is shifted in wave-length and obeys the simple quantum theory advanced by A. H. Compton and independently by P. Debye. Recently curves have been obtained which show that there is an appreciable wave-length breadth of the shifted radiation, as announced by Compton,[6] which cannot all be accounted for by the range of the scattering angle. Such an effect has been theoretically treated by Jauncey[13,14,15] and ascribed to the binding of the electrons to the nucleus and their motion in the Bohr orbits in the atoms of the scattering substance.

The early, unpublished work by Bergen Davis and the photographs taken by Ross lead to the conclusion that the ratio of the intensity of the modified line to the unmodified decreases with increasing atomic number, and the experiments reported here support this conclusion.

The investigation of the scattering of molybdenum rays by heavy elements is made difficult by the extremely low intensity of the *scattered* radiation from these elements. Thus in our experiments on Mg and S, the intensity of the scattered radiation was so small that reliable curves were obtained only with great difficulty. This effect may perhaps be ascribed to the rapid increase of true or fluorescent absorption with rising atomic number, while by comparison the scattering per electron remains approximately constant.

The question of the variation in the intensity ratio of the modified to the unmodified line with angle of scattering for a given element and given incident wave-length has been theoretically investigated by Jauncey.[14] The experiments reported here unfortunatly give no quantitative information on this interesting problem. Some experiments of Ross[16] seem to indicate that at small scattering angles the ratio of the modified to the unmodified line is decreased, and Compton[6] has also reported such an effect.

Experiments with Aluminium

The change of wave-length of the modified line with scattering angle is a fundamental part of the quantum theory of scattering advanced by A. H. Compton. Compton[6] has obtained curves showing this

[13] Jauncey, Phys. Rev. **24**, 204 (1924).
[14] Jauncey, Phil. Mag. **49**, 427 (1925).
[15] Jauncey, Phys. Rev. **25**, 314 (1925).
[16] Ross, Proc. Nat. Acad. Sci. **10**, 304 (1924).

effect in the scattering of Mo x-rays by carbon. In the present experiments a set of curves was obtained using aluminium radiators at various angles of scattering, and molybdenum primary rays. These are shown in Fig. 1. Simplified diagrams, showing to scale the relative positions

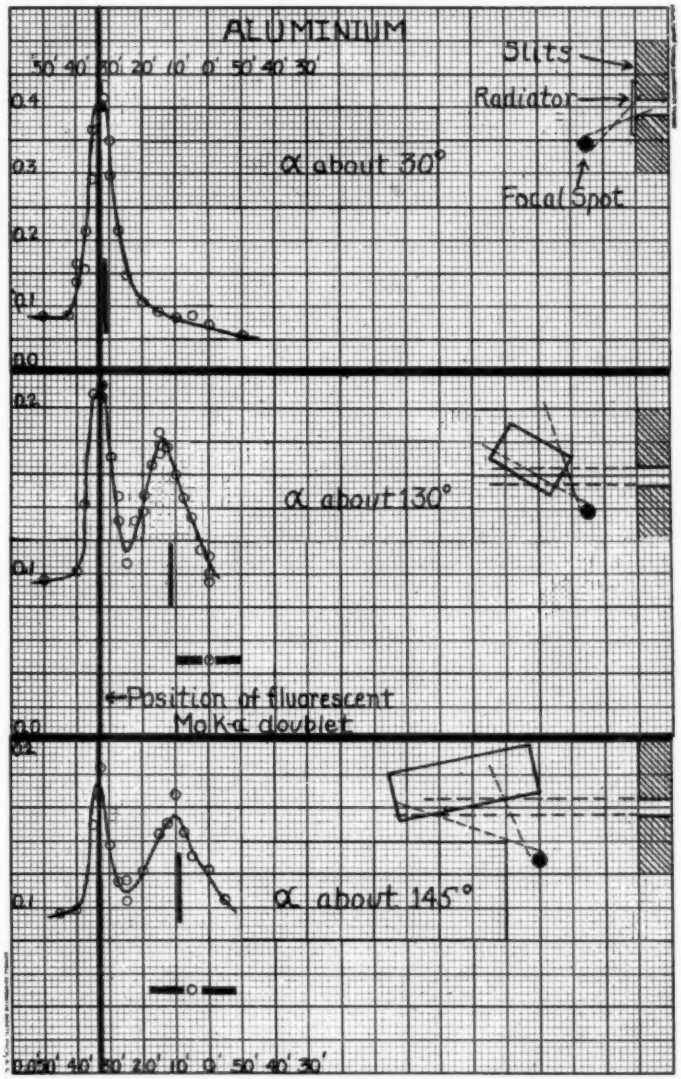


Fig. 1. Intensity distribution of x-rays scattered from Al at various angles.

and sizes of the scatterer, focal spot, and first slit appear at the right. The experiments were performed at a constant storage battery voltage

of about 40 kv and 20 m-amp. of current. The spectrometer scale was frequently calibrated by determining the position of the fluorescent molybdenum Kα doublet from a strip of molybdenum mounted in place of the scatterer. The position of this peak remained unchanged throughout the course of the experiments with aluminium and is indicated in the figure. The points below the curves taken at larger scattering angles show the ionization current obtained when the beam reflected by the crystal did not enter the ionization chamber slit. They therefore represent the height of the baseline due to natural leak of the electrical apparatus and to x-rays scattered by the crystal as an amorphous substance, etc. The position of the modified peak calculated from the Compton equation

$$\lambda - \lambda_0 = .0242 \quad (1 - \cos\alpha)$$

is shown by a heavy vertical line in each case. Since the finite size of the focal spot and radiator made quite a range of scattering angles possible, the position of the modified line agrees within experimental error with that predicted by the quantum theory of scattering.

It may be demonstrated from these curves that the intensity of the unmodified line relative to the general radiation under it is less than in the case of the radiation from the target direct. This ratio depends on the slit widths and the voltage. From the central curve of Fig. 1 ($\alpha = 130°$) the value 3 to 1 may be calculated for this ratio. Spectra obtained from the target direct with the same slit width and voltage show that in this case the ratio is much greater, being about 18 to 1. The reason for this difference is not yet quite clear.

Fig. 2 shows the curve obtained when the range of scattering angle is large and includes the region about 90° where the wave-length of the modified line is changing most rapidly. Here every small volume of the radiator in the path of the slit is emitting an unmodified ray of constant wave-length, and a modified ray of a wave-length which depends on its scattering angle. Under these conditions, the theory indicates, and the experiment shows, that the shifted radiation is drawn out into a band whose intensity is low compared to that of the unmodified ray. This illustrates the difficulty in obtaining evidence of the Compton effect with large radiators.

In Fig. 2 and in every curve reproduced, *all* the readings of one experiment are plotted that were obtained in the angular range through which the curve extends. Due to mechanical or electrical disturbances of some kind, whose effects were appreciable relative to the very low

intensities in the spectrum of the scattered x-rays, readings were occasionally obtained (as in Fig. 2) which were difficult to include in a smooth curve. Such readings were repeated later, as is indicated by two or more points for the same angular setting, and almost invariably then gave values consistent with the general trend of the curve.

Experiments with Lithium

A set of curves similar to those of Fig. 1, but with lithium as the scattering substance is shown in Fig. 3. The much greater intensity of the modified line with respect to the unmodified is at once apparent. These experiments were performed with two single slits defining the

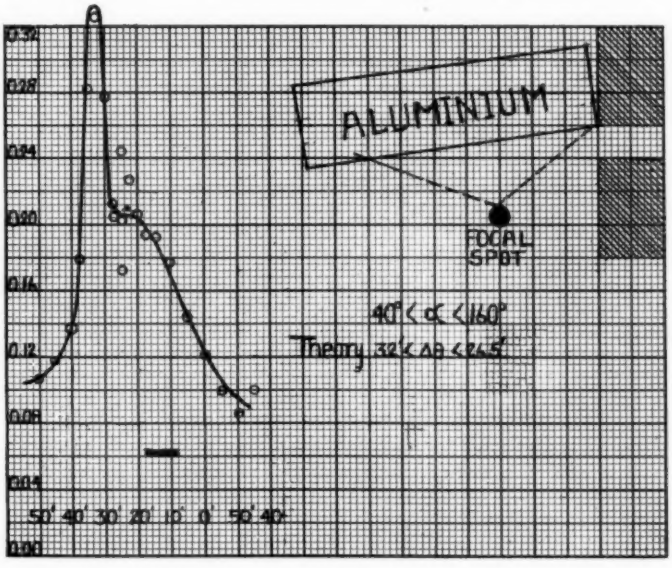


Fig. 2. Intensity distribution when the range of scattering angle is large.

beam. The results agree closely with those of similar experiments performed with multiple slits. With lithium as a scattering substance the intensity is much greater than with aluminium, and the curves, therefore, are more reliable. The lithium used appeared to be fairly free from oxide, and was kept coated with a paraffin oil during these experiments. The scattering from the carbon in this oil may have affected the relative intensity of the two lines somewhat. The slight shelf in the curve in which the angle of scattering is about 100° at the position of the unmodified peak was repeated several times and is undoubtedly present.

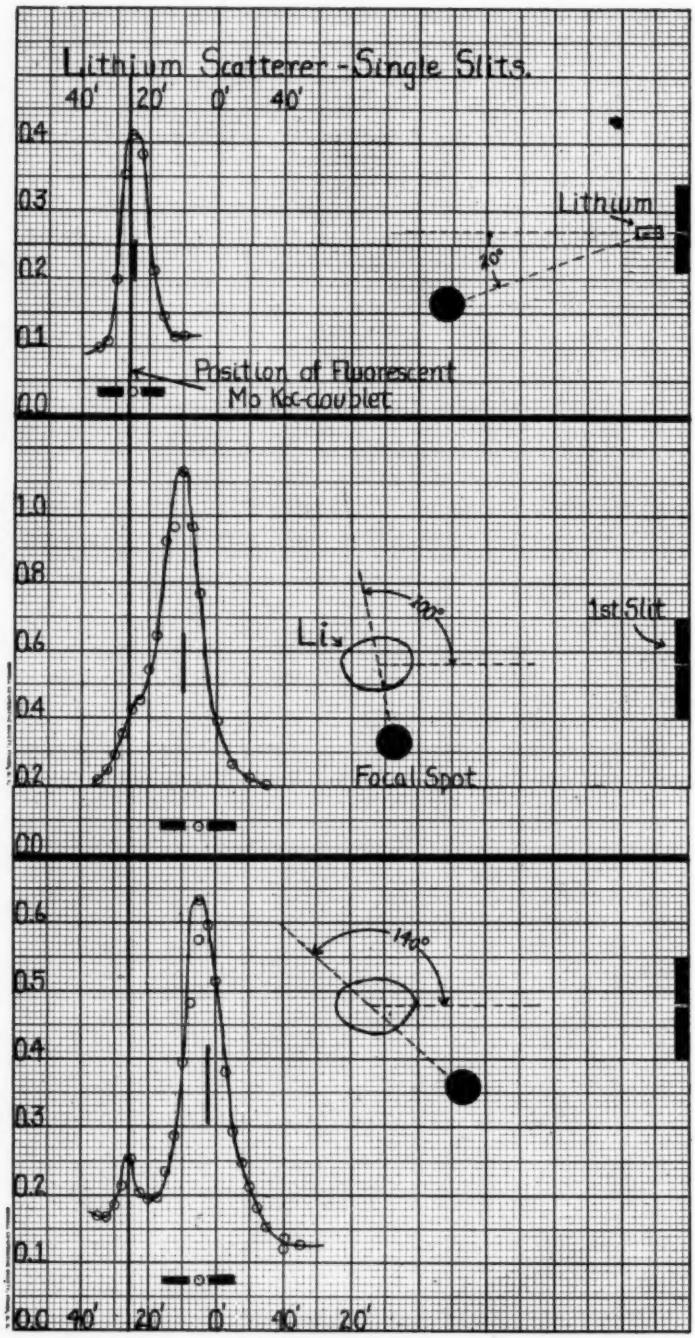


Fig. 3. Curves for scattering from lithium.

Experiments with Tungsten Primary Rays

Spectrometer measurements on the scattering of tungsten rays have been reported by Compton[6] and by Ross.[17] Ross has found that the relative intensity of the modified line to the unmodified for a given element is much greater for tungsten rays than for molybdenum rays. M. de Broglie[18] has reported measurements of the Compton effect using tungsten primary rays.

We have not found it possible as yet to operate a narrow x-ray tube with a tungsten target at sufficient voltages to bring out the tungsten

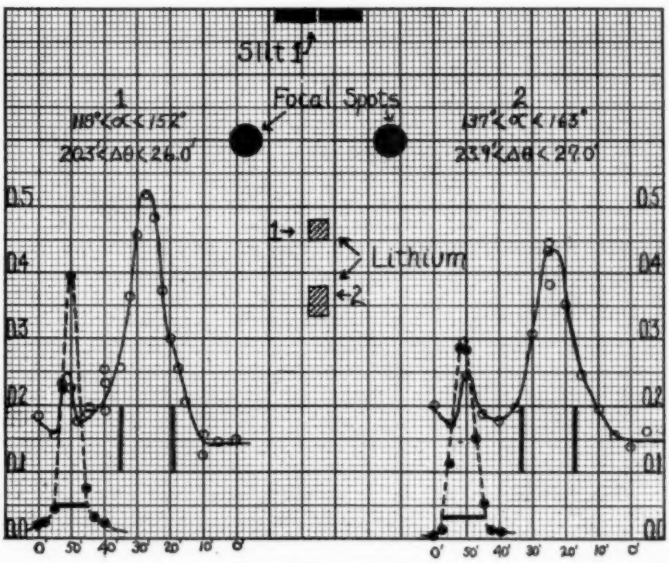


Fig. 4. Scattering from lithium irradiated from two Mo targets simultaneously.

characteristic rays strongly. Our experiments indicate that if this could be done, large intensities could be easily obtained. We have used a Universal type tube, operated at 100 kv and 6 m-amp. With this tube the radiators could not be placed nearer than 10 cm to the target. When the multiple slits were used, the rays were reflected internally from a thin slab of calcite placed across the beam. This solved the difficulty of obtaining a crystal long enough to take in the full beam by surface reflection at the small glancing angles involved. Aluminium and graphite radiators were used. The curves obtained were of low intensity, and not reliable as to details of shape, but showed

[17] Ross, Phys. Rev. **25**, 235 (1925).
[18] De Broglie, Compt. Rend. **178**, 908 (1924).

that the radiation was shifted as expected, and that the relative intensity of the shifted peak was greater for a given element than in the scattering of molybdenum rays, as reported by Ross.

The Breadth of the Shifted Line

Experiments have been recently performed in which the radiator was irradiated from two molybdenum target tubes simultaneously. Some curves that have been obtained are shown in Fig. 4. The curve marked 1 was taken when each tube was running at 47.5 kv and 20 m-amp. from the storage battery. Curve 2 was taken at about 40 kv and the same currents. The relative positions of the tubes, radiator, and slit are shown on the diagram. Single slits were used. The diagram refers to a horizontal plane through the top of the slit, which was 2.5 cm high.

With the extra intensity supplied by the second tube, it was possible to use smaller radiators than before, from which we could make a good estimate of the maximum range of scattering angle possible. In making this estimate, we have assumed that the entire button of molybdenum in the target of the tube acted as a source of x-rays, and have taken account of the vertical dimension of the slit in calculating the minimum scattering angle possible.

The width of the slits was calibrated by taking the fluorescent radiation from a molybdenum plate. This is shown in dotted lines. The heavy lines at the base of the fluorescent peaks show the angular widths at which the excess intensity due to the characteristic lines has fallen to about 1/20th of its value at the maximum. From this width, and the minimum and maximum scattering angles permissible, the angular range in which the modified peak should rise and fall to 1/20th its value above the general radiation have been calculated from the simple Compton equation. These angular ranges are between the vertical lines underneath the modified peaks. It seems evident that the modified peak is broader than that predicted by the simple Compton theory, extending certainly to longer wave-lengths than Compton's equation permits. This effect is presumably connected with the binding of the electrons to the nucleus,[13] and therefore should be less marked in lithium than in other heavier elements. The high intensities obtainable from lithium, however, have made the use of this element desirable.

It appears on consideration that all the experiments reported here contain a slight element of uncertainty in view of the fact that methyl iodide was used in the ionization chamber and the second order of the

iodine critical ionization wave-length occurs in the region of the shifted peak from Mo $K\alpha$. This observation applies to all the experiments of previous observers in which ionization measurements were made with methyl iodide gas. The curves taken at small scattering angles (Fig. 1) indicate fairly well, however, that such an effect is practically negligible. The extent of the discontinuity introduced into the baseline depends on the fraction of the energy in the iodine critical absorption wave-length (.3737A) which is absorbed in the chamber. It is very much smaller in second order reflections than in first.

These experiments indicate that the shifted radiation should be considered to be a band with a sharp intensity maximum which obeys the laws deduced from the simple quantum theory of the scattering by free electrons. In any given atom, the rays scattered by the loosely bound electrons may be considered to give the modified radiation obeying more or less approximately the simple Compton equation. The rays scattered by the more firmly bound electrons may well produce the major part of the unmodified line and contribute most of the breadth of the shifted line in excess of that due to the range of scattering angle.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
Cambridge, Mass.
May 26, 1925.

SERIES SPECTRA OF TWO-VALENCE-ELECTRON ATOMS OF BORON (B_{II}) AND CARBON (C_{III})

By I. S. Bowen and R. A. Millikan

Abstract

Series spectra of B_{II} and C_{III}.—By methods previously reported in the identification of lines in the extreme ultraviolet, 13 lines in addition to the pp' group of B_{II} have been identified, completing the classification of all lines known to be due to B_{II}. Taking the $4f$ level as 27800 (probably correct to within 200 frequency units), the following term values were obtained for B_{II}: $3s$, 72930.8; $4s$, 36655.5; $2p_1$, 165343.9; $2p_{2,3}$, 165362.7; $3p_1$, 59006.5; $3p_{2,3}$, 59010.0; $3d$, 52054.2; $4d$, 28640.4; $5f$, 17795.7; $2S$, 194325.9; $3S$, 66665.1; $2P$, 120929.4; $3D$, 48410.3. In the case of C_{III}, 8 lines in addition to the pp' group were identified, and taking the $4f$ level as 62600, the following term values were obtained for C_{III}: $3s$, 146197.2; $2p$, 331939.2; $3p_1$, 124685.8; $3p_2$, 124698.6; $3p_3$, 124704.1; $3d$, 114387.2; $2S$, 375463.1; $2P$, 273111.0.

Progression of frequency separations and of screening constants for regular doublets for Li to O is shown in Table VI, for one to six valence electrons. The separation $(2p_2-2p_1)$ or $(2p_3-2p_1)$ regularly decreases and the constant s regularly increases, for a given element, with the number of valence electrons, irrespective of the fact that both doublets and triplets are involved.

1. Identification of B_{II} Lines

THE term-values of the stripped, or one-valence-electron, atoms of boron (B_{III}) and carbon (C_{IV}) have recently been worked out and published.[1] In the case of two-valence-electron atoms of these elements we have observed and published the characteristics of their pp' groups,[2] and have thus fixed with accuracy the frequency separations of the three $2p$ levels, viz. $2p_1$, $2p_2$, $2p_3$.

But as soon as these separations are known it becomes possible to identify the boron lines which arise from jumps into these $2p$ levels. Thus the separation between $2p_1$ and $2p_3$, i. e., the total width of the triplet, is actually the distance between the second and the last components of the pp' group, numbering from the short wave-length side. This was found from the pp' plates to be 22.8^{-1} for B_{II}.

The first member of the diffuse series of B_{II} $(2p-3d)$ ought to be located at a wave-length a little larger than the corresponding line of stripped boron (B_{III}) which was before found at λλ677.01, 677.16.

[1] Bowen and Millikan, Proc. Nat. Acad. **10**, 199 (1924), and Nature **114**, 380 (1924).
[2] Towen and Millikan, Phys. Rev. **26**, 150 (Aug. 1925).

The only strong line on our plates in approximately this position is the line the wave-length of which we had published as 882.3A. In this region the foregoing separation would amount to but 0.18A. Since the p_2p_3 separation was less than a third of this we could not hope to resolve all three of the $(2p-3d)$ lines but could expect to obtain a resolution that would bring to light a doublet with a separation equal to the distance of p_1 from the center of gravity of p_2 and p_3.

We accordingly sought to obtain a spectrogram of the fifth and sixth orders of the line 882.3A. In both these orders it appeared as a doublet, as predicted, with a frequency separation of 18.3 cm^{-1}. Since this is definitely different from the characteristic separations of both B_I and B_{III} it can only be due to B_{II}. Again, the $(2p-3s)$ line of B_{II} must reveal the same separation as the foregoing but should have a slightly longer wave-length. Our next strong line, namely that at λλ1081.88, 1082.10, showed as a doublet in the fourth and fifth order spectra with a measured separation of 19.3 cm^{-1}, in agreement within the limits of error with the foregoing.

The next jump most likely to occur is the $(3d-4f)$. This jump is between two remote circular orbits and its value may be computed roughly by multiplying the corresponding line for hydrogen by four. This gave λ4688. The only unidentified line of any strength in this region was that at λ4122.99, which was accordingly taken as the line sought.

The $4f$ level for B_{II} would have a frequency value, if it were completely hydrogen-like, of $109732/4=27433$. The corresponding value for two-valence electron aluminum (Al_{II}), which is certainly less perfectly screened than B_{II}, is 28440. The $4f$ term-value for B_{II} had to lie between these limits and was taken as 27800, the uncertainty being not more than two or three hundred frequency units. With the aid of this starting point and the foregoing lines the $3d$, $2p$, and $3s$ levels were at once obtained as shown in Table I. The line $(3s-3p)$ has not yet been observed, but a fairly accurate prediction as to its frequency can be made from the frequency of the corresponding line in C_{III} and the progression of the Mg_I to S_V series.[3] By taking this line as having a frequency 13920, the $3p$ level was obtained from this frequency and the already-determined $3s$ level. The jump $(3p-4s)$ was found by looking for another doublet having the $3p$ separations. This was found at λλ4473.37, 4474.08, and this fixed the $4s$ level shown in the table.

[3] Bowen and Millikan, Phys. Rev. **25**, 594 (1925).

The B_{II} singlet series was worked out as follows. By comparison with the $3S-3P$ lines of the series Mg_I to Cl_{VI} and the already located $2S-2P$ line of Be_I,[4] viz., 2348.70, it was seen that $2S-2P$ for B_{II} should fall at about 1400A. The only very strong line in this region, in fact the strongest unidentified boron line below 3000A, was 1362.46A. This could scarcely be any other than $2S-2P$. The next strongest

TABLE I

Series lines for B_{II}

Int.	λ(I.A., vac.)	ν	Δν		Term values	
0	731.46	136712.9		$2p-4d$	$3s$	72930.8
3	882.55	113308.2		$2p_{2,3}-3d$	$4s$	36655.5
			> 18.3			
3	882.69	113289.9		$2p_1-3d$		
					$2p_1$	165343.9
3	1081.88	92432.1		$2p_{2,3}-3s$	$2p_{2,3}$	165362.7
			> 19.3			
3	1082.10	92412.8		$2p_1-3s$	$3p_1$	59006.5
					$3p_{2,3}$	59010.0
8	1362.46	73396.5		$2S-2P$		
3	1378.95	72519.1		$2P-3D$	$3d$	52054.2
4	1623.66	61589.2			$4d$	28640.4
4	1623.86	61581.7				
5	1624.08	61573.2		pp' group		
4	1624.25	61567.0			$4f$	27800.0
4	1624.46	61558.9				
					$5f$	17795.7
5	1842.83	54264.3		$2P-3S$		
2	2918.98	34258.5		$3d-5f$	$2S$	194325.9
10	3452.33	28965.9		$2S-2p_2$	$3S$	66665.1
6	4122.99	24254.2		$3d-4f$		
					$2P$	120929.4
1	4473.37	22354.5		$3p_{2,3}-4s$		
			> 3.5			
1	4474.08	22351.0		$3p_1-4s$	$3D$	48410.3

lines to be expected were the $(2P-3D)$ and the $(2P-3S)$, the former of which should have the shorter wave-length. The only unidentified boron lines below 3000A, were[5] now λ1378.95 and λ1842.83, the first of which should therefore be $(2P-3D)$ and the second $(2P-3S)$. This fixes every known boron line of any strength except the familiar

[4] Paschen and Götze, Seriengesetze etc., p. 71.

[5] The line λ1378.95 did not appear in our original list of boron lines (Phys. Rev. **23**, 7, 1924) because, with the resolution then used it was not separated from the strong aluminum line at λ1379.7. With our present high-resolution the two lines are very easily seen to be distinct.

and exceedingly powerful line at $\lambda_{vac}=3452.33$ which, in conformity with the behavior of all two-valence electron systems is $(2S-2p_2)$. This connects the singlet and triplet systems, the latter of which have been worked out above; i. e. $2p_2$ being known, this last line fixes the value of $2S$, and from this all the other singlet levels come out at once from the foregoing relationships with the values given in Table I.

The present work then completes the identification of all the known boron lines of any intensity and the classification into series of all the lines due to B II and B III.

2. Method of Identification of C III lines

One of the chief contributions of our development of hot-spark spectrometry to the identification of spectral lines has arisen from the fact that with these hot sparks we have been able to obtain for comparisons in the optical region a long series of atoms of varying nuclear charge but of like electronic structure and have found through such comparisons that such series follow the Moseley law quite as well in the field of optics as in the field of x-rays. The analytical expression of this law is

$$\frac{\nu}{R}=\left(\frac{Z-\sigma}{n}\right)^2 \tag{1}$$

in which ν is the energy of the orbit expressed in terms of a frequency, Z the atomic number, σ the screening constant and n the total quantum number. We have already pointed out that the frequency ν' of a spectral line due to an electron jump between two such orbits which have different screening constants σ_1 and σ_2 respectively must be given, with entire generality, by

$$\frac{\nu'}{R}=\left(\frac{Z-\sigma_1}{n_1}\right)^2-\left(\frac{Z-\sigma_2}{n_2}\right)^2 \tag{2}$$

or

$$\frac{\nu'}{R}=\frac{(n_2^2-n_1^2)Z^2-2(n_2^2\sigma_1-n_1^2\sigma_2)Z+n_2^2\sigma_1^2-n_1^2\sigma_2^2}{n_1^2\,n_2^2} \tag{3}$$

an equation which shows, as previously pointed out, that when, and only when n_2 is equal to n_1 and σ_1 and σ_2 are independent of Z, do the frequencies ν' progress linearly with atomic number Z, i. e., follow the irregular doublet law.

In seeking to use these relations for the prediction of the positions of the spectral lines of C III we observe first that the strongest C III line to be expected at all is the first term of the principal series of singlets,

viz. $(2S-2P)$ and, since for this line $n_2=n_1$ and σ_1 and σ_2 may be expected to be independent of Z, there should be here a linear progression of ν' frequencies with atomic number, a prediction which we have always found experimentally verified in the case of all lines that are due to jumps between orbits of the same total quantum number. Table II gives in its first two rows the frequencies of this line for two-valence-electron beryllium (Be_I) and boron (B_{II}) and enables us definitely to locate $(2S-2P)$ for C_{III} at approximately $73000+30000=103000$, which corresponds to $\lambda 971$. This identifies the very strong carbon line 977.02 as the $(2S-2P)$ line of C_{III}, for our plates taken with high resolution reveal this as the only singlet carbon line of any strength within a hundred angstroms of the predicted wave-length.

TABLE II

Irregular doublets, $2S-2P$

	Frequency	Diff.
Be_I	42565.1	
		30831.4
B_{II}	73396.5	
		28955.6
C_{III}	102352.1	

The next strongest C_{III} lines should be $(2p-3d)$ and $(2p-3s)$. It is, however, impossible to locate them by means of the irregular doublet law, since, n_2 being here different from n_1, this law can no longer hold. Eq. (3), however, is of general validity and gives the actual variation of ν' with Z if only σ_1 and σ_2 are not functions of Z, as has been shown to be the case by the observed linear relation between ν' and Z when $n_1=n_2$.

Also (3) may be written

$$\nu'-RZ^2(n_2^2-n_1^2)/n_1^2n_2^2=CZ+D \qquad (4)$$

where C and D are constants so long as we are considering a given sort of electron-jump, i. e., a given set of values of n_2, n_1, σ_1, and σ_2. The quantity on the left will then show a linear progression with Z.

To transform this expression into one slightly more convenient for use we substitute $(Z-A)$ for Z and get

$$\nu'-R(Z-A)^2(n_2^2-n_1^2)/n_1^2n_2^2=C'Z+D' \; . \qquad (5)$$

The left side is again a quantity which varies linearly with Z and from which ν' may be predicted for any value of Z as soon as any two other values have fixed C' and D'. For the case in hand $n_2=3$, $n_1=2$ and hence

$$R(n_2^2-n_1^2)/n_1^2n_2^2=109732(9-4)/[9\times 4]=15240.55 \; . \qquad (6)$$

We are here dealing with the progression with atomic number in the

frequency of a particular line found in the spectra of beryllium, boron, and carbon. Hence to make $(Z-A)$ conveniently small we shall take $A=3$. Then with the use of Paschen and Götze's value of ν' for $2p_2-3d$ in beryllium (Be_I) and our own value, determined above, of the same line in B_{II} we obtain the first two numbers under column 2, Table III. The first two numbers of column 3 are obtained by subtracting 1 and 4 times 15240.55 respectively from these two frequencies in column 2. The numbers in column 3, which now represent the left side of Eq. (5), should progress linearly with Z, and hence the difference between them (first number in column 4) added to the second in column 3 should give the left side of Eq. (5) for C_{III}. By adding 9×15240.55 to this we obtain the frequency of $2p-3d$ for C_{III}. The result thus obtained is found to fall within 500 frequency units, or about 1 angstrom, of the strong carbon line at λ459.7. The data given under C_{III} in Table III are the *observed* values corresponding to this line and show how nearly linear is the actual progression.

TABLE III

Progression with atomic number of the frequency of $(2p_2-3d)$ and $(2p_2-3s)$

		ν	$\nu-(5/36)(Z-3)^2R$	Diff.
$2p_2-3d$	Be_I	40075.13	24834.58	
				27511.42
	B_{II}	113308.2	52346.0	
				28041.0
	C_{III}	217552.	80387.	
$2p_2-3s$	Be_I	30100.88	14860.33	
				16609.57
	B_{II}	92432.1	31469.9	
				17107.1
	C_{III}	185742.	48577.	

By precisely the same procedure, using the $(2p-3s)$ frequencies for Be_I and B_{II}, we obtain the lower half of Table III and identify the strong carbon line λ538.4 as $2p-3s$ for C_{III}.

The next strong line to be sought in C_{III} would naturally be $(3d-4f)$ and since this is a jump between two fairly remote circular orbits it should be approximately hydrogen-like and hence have an approximate frequency 9 times, or a wave-length one-ninth of, the value for the corresponding line (λ18751) in hydrogen. The result is λ2083, which identifies with sufficient accuracy the strong carbon line at 1930.98 as $(3d-4f)$ for C_{III}.

The carbon triplet at λλ4648.70, 4651.46, 4652.65, long ago found in the hottest stars (O type stars), obtained also in the laboratory by

Merton in 1915,[6] has already been classified as belonging to C_{III} because it does not appear in the arc spectrum, and, being a triplet, can therefore not belong to any stage of ionization of carbon other than C_{III}. It is here for the first time identified as $3s-3p$ by the fact that its position is about right[7] for $3s-3p$ and by the further fact that the separations of its components require it to be a line of a principal series and there is no other principal series triplet of suitable intensity.

The very strong carbon line at 2297.59 we identify as $2S-2p_2$, first by elimination—all of the other C_{III} lines that may be expected to be strong have already been identified and this line must belong to C_{III} since it is definitely a spark line and is not in Fowler's group of C_{II} lines; second, roughly by position—the $2S-2p_2$ line in B_{II} being at λ3452.33, the corresponding line in C_{III} may be expected to be somewhere between 2000 and 3000A; third, by its characteristics—this line comes out very easily for so high a stage of ionization and this is characteristic of the $2S-2p_2$ line wherever it appears.

TABLE IV

Series lines for C_{III}

Int.	λ(I.A., vac.)	ν	$\Delta\nu$		Term values	
6	459.7	217552.		$2p-3d$	$3s$	146197.2
7	538.4	185742.		$2p-3s$	$2p$	331939.2
12	977.02	102352.1		$2S-2P$	$3p_1$	124685.8
4	1174.96	85109.0			$3p_2$	124698.6
4	1175.31	85084.2			$3p_3$	124704.1
5	1175.72	85054.0		pp' group		
4	1176.03	85031.6				
4	1176.40	85005.1			$3d$	114387.2
7	1930.98	51787.2		$3d-4f$	$4f$	62600.
10	2297.59	43523.9		$2S-2p_2$		
3	4648.70	21511.4		$3s-3p_1$	$2S$	375463.1
			>12.8			
2	4651.46	21498.6		$3s-3p_2$	$2P$	273111.0
			> 5.5			
1	4652.65	21493.1		$3s-3p_3$		

We have sought without success on our plates for the other singlet lines of C_{III} which might be expected to be strong, such, for example, as $2P-3D$ and $2P-3S$. This failure might possibly raise some question

[6] Merton, Proc. Roy. Soc. **91**, 498, (1915).

[7] $(2p-3d)-(2p-3s)=3s-3d=31810$ (see above), and $3s-3p$ should be about 2/3 of $3s-3d=21000$ cm^{-1} or at λ 4762.

about some of the other identifications, although it is in keeping with the fact that Fowler has been unable to find the corresponding lines in Si III.

The starting point for obtaining the series of C III levels from the foregoing lines was taken, as in the case of B II, as close to the theoretical hydrogen-like value for $4f$. This hydrogen-like value for C III should be $109732 \times (9/16) = 61724.3$. We arbitrarily took, as in the case of B II, a value a trifle higher than this, namely 62600, and then obtained at once from this and the foregoing line-frequencies the term-values given in Table IV.

TABLE V

Comparison of term values

	$N=$	2	3	4
	$R/N^2=$	27433.0	12192.3	6858.3
s	B/4	.....	18232.7	9163.9
	C/9	.....	16244.1	
p_1	B/4	41336.0	14751.6	
	C/9	36882.1	13854.0	
d	B/4	.....	13013.6	7160.1
	C/9	.....	12709.7	
	B/4	.....	.....	6950.
	C/9	.....	.....	6955.6
S	B/4	48581.5	16666.3	
	C/9	41718.1	.....	
P	B/4	30232.4	.....	
	C/9	30345.7	.....	
D	B/4	.....	12102.6	

Table V is added to conform with the general scheme of comparison of term-values that we have heretofore used, following Paschen and Fowler.

3. Effect upon the Force Field within the Atom of the Successive Addition of Electrons to the Valence Shell

We have added a further Table VI for the sake of exhibiting even more strikingly than we have heretofore done, first, the systematic progression of the value of the screening constant s of the regular-doublet law as each new electron is added to the valence shell, and, second, the fact that the triplets behave precisely as do the doublets in systems of like electronic structure and varying nuclear charge.

The upper half of the table gives the $(2p_2-2p_1)$ doublet-separations in the first, third, and fifth columns, for one, three, and five electron systems, respectively, and the $(2p_3-2p_1)$ triplet separations in the second, fourth and sixth columns, for two, four, and six electron systems. For the two-valence electron systems these separations are obtained from the pp' groups. The lower half of the table gives the values of the screening constant s as computed from the regular doublet law as outlined in Physical Review **24**, 209 (1924). The table shows very

TABLE VI

Frequency separations and screening constants for regular doublets and triplets

Electrons =	1	2	3	4	5	6
	$(2p_2-2p_1)$	$(2p_3-2p_1)$	$(2p_2-2p_1)$	$(2p_3-2p_1)$	$(2p_3-2p_1)$	$(2p_3-2p_1)$
Li	.338					
Be	6.61	3.02				
B	34.1	22.8	15.55			
C	107.4	79.1	66.76	46.8		
N	259.1	204.1	179.3	132.2	85.3	
O	.....	459.5	398.4	309.0	....	224.0
	Screening constant $s=Z-\sqrt[4]{\Delta\nu/.365}$					
Li	2.019					
Be	1.937	2.304				
B	1.884	2.189	2.445			
C	1.858	2.163	2.332	2.635		
N	1.838	2.137	2.292	2.638	3.090	
0	.....	2.043	2.252	2.606	.....	3.023

beautifully the effect upon the force-field about the nucleus of the successive addition up to six of each new valence electron to the valence shell. The progression is at least qualitatively quite such as is to be expected from the successive introduction into the atom of six point charges each endowed with a coulomb field.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA.

June 6, 1925

THE ISOTOPE EFFECT IN BAND SPECTRA, IV: THE SPECTRUM OF SILICON NITRIDE

By Robert S. Mulliken[1]

Abstract

Silicon nitride bands.—(1) A system of bands shaded toward the red, lying between 3800 and 5300A was obtained by Jevons in 1913 by the introduction of $SiCl_4$ vapor into active nitrogen. His measurements have been repeated and extended to all possible heads. It is important that no oxygen be present. From a sharp intense head each band decreases rapidly in intensity to zero at the null line, then increases to a maximum at about $m=13$ in the negative branch, in which the lines get far enough apart to be resolved. With the aid of the quantum theory, Jevons' arrangement was revised, and correct initial (n') and final (n'') vibrational quantum numbers assigned. The null lines of the $Si^{28}N$ bands correspond to the wave-number equation: $\nu^\circ = 24234.2 + 1016.30\ n' - 17.77n'^2 + 0.410n'^4 - 0.00487n' - 1145.00n'' + 6.570n''^2$. Partial analysis of the band structure indicates that the lines of any band are given by the equation: $\nu = \nu^\circ + B' + 2B'm + Cm^2$ where $B' = 0.728 - 0.097n'$ and $C = -0.0121 - 0.0097n' + 0.0053n''$; from this the internuclear distance for the vibrationless SiN molecule is 1.56×10^{-8} cm. Additional weak heads are present whose positions agree very closely with those calculated for the isotopes $Si^{29}N$ and $Si^{30}N$, isotope 29 being slightly the stronger. This agreement definitely excludes SiO or any other compound than SiN as the emitter of the bands, confirming the chemical evidence. The agreement is also definite, but not conclusive, evidence against the existence of half-quantum numbers for SiN, a result opposite to that for BO. Plate I shows most of the $Si^{28}N$ bands together with some isotope heads. The intensity distribution in each band corresponds to thermal equilibrium at about 80°C. In respect to the initial vibrational quantum number, the distribution is non-thermal and corresponds to a high effective temperature as in other cases such as BO and CN. The intensity distribution with respect to Δn is similar to that of the violet CN bands. The sequence $\Delta n = 0$ is by far the strongest, other sequences of diminishing intensity being observed as far as -3 and $+3$ or $+4$. (2) *New system of bands*, extensive but weak, probably also due to SiN, is described. They all have double heads ($\Delta\nu = 27$), are shaded toward the red and extend from the ultraviolet through the green. An equation for the heads is given. The intensity distribution is characterized by numerically large values of Δn and by the absence of the band $(0 \rightarrow 0)$ and some neighboring bands.

Introduction

In 1913 Jevons described[2] an interesting band spectrum obtained by the introduction of silicon tetrachloride vapor into active nitrogen, and consisting in a system of bands, shaded toward the red, lying in

[1] National Research Fellow.

[2] W. Jevons, Roy. Soc. Proc. **89A**, 187 (1913-14).

the region between λ3800 and about λ5300. Jevons ascribed the bands to a nitride of silicon, this being supported by the fact that they were not obtained by the discharge through pure $SiCl_4$ and by the further fact that a nitrogen-containing product was deposited on the walls of the nitrogen afterglow tube during the emission of the bands. As Jevons pointed out, the action of active nitrogen on $SiCl_4$ is similar to its action on carbon compounds, the cyanogen bands being emitted in the latter case. Many of the bands, according to Jevons, show a minimum of intensity about 4A from the head, a similar phenomenon being observed in the cyanogen bands when produced in active nitrogen. Jevons arranged all the bands in rows and columns such that the successive intervals of frequency taken vertically and horizontally form arithmetical progressions (the intervals being substantially constant in a given row or column of frequency-intervals), and from these he determined the constants of a Deslandres equation.

In addition to the data on the heads of the silicon nitride bands, Jevons gives a list of silicon lines which are emitted at the same time. In the present work, one additional Si line was found, that at λ4103.1, and possible indications of one or two others.

In the light of the quantum theory of band spectra, it is now evident that the intensity minimum observed by Jevons in many of the bands must represent the region of the null-line, or missing line, which is of much more importance from a theoretical standpoint than the usually much more obvious head. The unusual prominence of the null-line here must be ascribed to the low temperature of active nitrogen; this subject has been discussed by Birge in the analogous case of the cyanogen bands.[3] The null-lines are plainly visible in two of the bands in Jevons' reproductions, and are particularly well brought out in photographs taken by the present writer (cf Plate I). The structure of the bands is of a simple type (probably like that of the violet cyanogen bands) which in the light of the quantum theory, shows that they are due to a diatomic emitter. That they are due to the compound SiN is probable from the chemical evidence (including that above cited and new evidence given below), and is definitely proved by the isotope effect (see below).

A re-examination of the silicon nitride spectrum was undertaken by the writer in 1923 with the object of studying the expected isotope effect. At this time Si was known from Aston's positive ray work[4]

[3] R. T. Birge, Astrophys. J. 55, 273 (1922).
[4] F. W. Aston, Isotopes, 2nd ed. p. 77 (1924).

to contain a small amount of an isotope 29 in addition to the dominant isotope 28; there was also doubtful evidence of an isotope 30 in small amounts, the doubt being occasioned by the possible presence of H compounds of the same mass-number. Jevons' data on the SiN bands evidently refer to $Si^{28}N$ heads, and include no measurements which can be attributed to $Si^{29}N$ or $Si^{30}N$ heads. New photographs by the writer showed clearly, however, that each favorably located $Si^{28}N$ head of sufficient intensity is accompanied by two approximately equally spaced weak satellites at the theoretically expected positions for $Si^{29}N$ and $Si^{30}N$, isotope 29 appearing to be slightly more abundant than isotope 30. This was reported in a letter to Nature.[5] The existence of isotope 30 was later confirmed by Aston by the positive ray method,[6] it being found slightly less abundant than 29, in agreement with the results on the SiN bands.

In order to determine the theoretical positions of the isotope heads, vibrational quantum numbers were assigned to the bands measured by Jevons, making use of the latter's arrangement of the bands in rows and columns, and merely changing his empirical numbers $m = 22, 21, \ldots . 12$ and $p = 55, 54, \ldots . 50$, to $n' = 0,1 \ldots . 10$ and $n'' = 0, 1, \ldots . 5$, n' being the vibrational quantum number of the initial electronic state of the molecule, n'' that of the final state. Measurements were also made on the null-lines, using Jevons' measurements on the heads as reference standards, and an equation for the null-lines in terms of n' and n'' was obtained.[7] On this basis, the isotope effect showed good agreement with theory for the final state of the molecule but was abnormally large for the initial state, especially for large values of n'; this anomaly was associated with various other peculiarities for the initial state, in particular with an extraordinary low vibration frequency as compared with that of the final state.[5,7] Complete new measurements of the heads and null-lines of the SiN bands were recently made, in order to be more certain as to the reality of the abnormal isotope effect, and in order if possible to find a means of avoiding it. With the new data, which differ considerably from those of Jevons in a few cases, the above arrangement of the bands in rows and columns now gives rather small, but definite and systematic, deviations from the constancy required by the combination principle for the frequency-intervals between neighboring rows, or neighboring

[5] R. S. Mulliken, Nature, March 22, 1924.
[6] F. W. Aston, Nature, Aug. 23, 1924.
[7] Paper presented before Am. Phys. Soc.; abstract in Phys. Rev. **23**, 554 (1924).

columns. By an arrangement of the bands differing radically from the old, it is found possible to satisfy completely the requirements of the combination principle and thus be sure that the new assignment of vibrational quantum numbers is correct. With this assignment, all the previous peculiarities and anomalies disappear and the isotope effect, in particular, is found to be in complete agreement with the theory. The former plausible but incorrect assignment is now seen to have been due to an unusual combination of misleading circumstances and relations. For the *heads*, it may be noted, the constancy of the frequency intervals is better with the old assignment; but this is of course of no theoretical importance.

Experimental Procedure in Production and Measurement of Bands

Production of bands; evidence on nature of emitter. The bands were obtained by the same general method as that of Jevons, using active nitrogen. In the latter part of the work, the same apparatus was used as in the work on the copper halide bands,[8] except that the bulb containing the silicon chloride, instead of being heated as in the case of the copper salts, was separated from the afterglow tube by a stopcock to control the flow of $SiCl_4$ vapor, $SiCl_4$ being a very volatile liquid. The $SiCl_4$ used was some material, free from CCl_4 in particular, which had been especially purified in connection with atomic weight work and which was kindly made available by Professor G. P. Baxter.

As noted in a previous paper,[9] the purple glow of the SiN bands is obtained in good intensity only when the nitrogen used is very free from oxygen, this behavior being in marked contrast to that of the BO bands and constituting strong evidence for the nitride origin of the present bands. Photographs were taken of an arc between silicon electrodes in an atmosphere of nitrogen in the hope of finding the SiN bands and getting additional evidence as to their nitride origin; but they were not present, perhaps because of a trace of oxygen impurity. The silicon arc in air gives oxide bands.[10] Apparently at high tem-

[8] R. S. Mulliken, Phys. Rev. **26**, p. 1 (July, 1925); cf. Fig. 1 and p. 7-8.

[9] R. S. Mulliken, Phys. Rev. **25**, 259-94 (1925). See p. 277.

[10] A. del Campo, An. Soc. Esp. de Fis. Quim. **13**, 98 (1913); A. del Campo and J. Estalella, ibid **20**, 586 (1922); C. Porlezza, Atti. accad. Lincei **31** (ii) 513 (1922), and Gazz. Chim. Ital. **53**, 215 (1923); W. Jevons, Roy. Soc. Proc. **106A**, 174 (1924). The bands, which are those of a diatomic emitter, are in all probability due to SiO, since the presence of oxygen is required (del Campo, Jevons). The heads can be represented by the equation (cf R. Mecke, Phys. Zeit. **26**, 239, 1925) $\nu = 42{,}643 + 844.5\ n' - 5.8\ n'^2 - 1236.0\ n'' + 6.04\ n''^2$.

peratures the affinity of silicon for oxygen exceeds that for nitrogen, while the fact that the carbon arc in air gives the CN bands indicates that the reverse is true for carbon.

New photographs and measurements. The photographs were obtained with the Hilger glass prism spectrograph used in previous work on BO and CuI, and all precautions were taken to secure the best possible definition. Greatly enlarged reproductions from one of the photographs are shown in Plate I. For the measurements, three photographs were used with a copper arc and three others with an iron arc comparison spectrum. Detailed measurements were made on one of these, and enough measurements on the others to make sure that they all gave consistent results, showing the absence of appreciable displacements in the comparison spectra. As in the case of the BO bands,[11] the results differed appreciably from those of Jevons, being consistently lower by 2−3 wave-number units in the region from λ3950 to λ4360, but differing irregularly in the region of longer wave-lengths, being for the most part a few or even several units higher. For the weaker bands, these differences may be ascribed to inaccuracy in Jevons' measurements, in accordance with his statement that the accuracy is low for these bands. The consistently lower present results in the short-wave-length region of stronger bands are more difficult to explain. In the case of BO, it was suggested that such a difference might arise if in Jevons' measurements the setting was made on the extreme high-frequency edge of the head, while in those of the writer it was made at the point of maximum blackening, the heads being treated like lines. A comparison of the two methods of setting for a number of the SiN bands gave an average difference for the two methods of about 0.010 mm, the difference being surprisingly constant for bands of greatly varying intensity and structure. Since this difference corresponds to an average of only about 1.1 wave-units with the dispersion used, the suggested explanation is evidently inadequate to account for the discrepancy between the present results and those of Jevons. No further attempts have been made to determine the cause of the discrepancy, since a possible small constant error is obviously of minor importance in the theoretical interpretation of the data. The data on heads given in the following tables were all obtained by the method of setting on the point of maximum blackening for each head.

Measurements were made on the heads of all possible $Si^{28}N$ bands. The ultraviolet was photographed with a quartz spectrograph, in order

[11] Mulliken, loc. cit[9], p. 267-8.

DESCRIPTION OF PLATE I.

Beginning with the top row, the reproductions show the entire SiN spectrum between λ3986 and λ4800. They were made in four sections from a single negative; each junction point is indicated by a dot *above*; in each successive section a somewhat more heavily exposed print was used than for its neighbor to the left in order to show both strong and weak heads to best advantage. Except for this (and an undue weakening of the bands at the high-frequency end due to prism absorption, and of the 7,9 band at the other end by decreasing plate sensitivity) the reproduction gives an essentially correct idea of the intensity distribution.

The *head* of each A band of $Si^{28}N$ is marked with a line, and the vibrational quantum numbers (n', n'') are given. In the case of the more intense bands, the fall of intensity from the head to the null-line, and the rise to a maximum in the negative branch before the final fading out, are well shown. The weak $Si^{29}N$ and $Si^{30}N$ heads, which are at the left of the corresponding $Si^{28}N$ heads, are marked when visible. The pairs of dots under the lowest section of the plate indicate the positions of the heads of some of the *new* bands; beginning at the left, the (1,5), (0,5), (1,6), and (2,7) head-pairs are marked; of these (1,5) is the most clearly visible. Unmarked conspicuous heads or lines (aside from structure lines of the bands) are of unknown origin (cf Table VI).

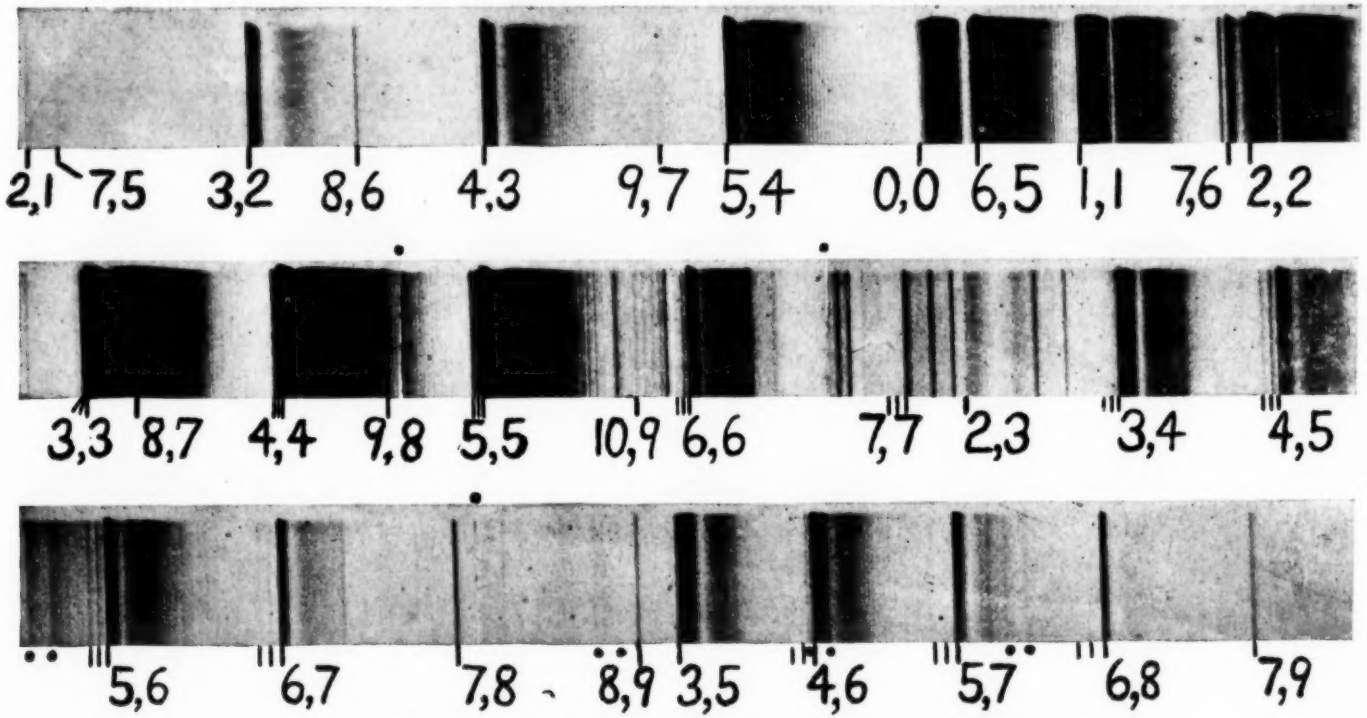


PLATE 1. The entire band spectrum of SiN from λ3986 (top) to λ4800 (bottom).

to measure a few heads which were not transmitted by the glass prism. Some new bands of a different type were also found; other new bands were also found in the green (see later section).

The *null-lines* of as many SiN bands as possible were measured on the plates, the setting being made at the point of minimum intensity. In some bands where the head is at a considerable distance from the null-line, the latter appears as a distinct narrow gap in the shading; in others where it is nearer, as a mere lightening; these effects can be seen in the reproductions (Plate I). Settings on the null-lines are subject to rather greater uncertainty than in the case of heads, but it is thought that the data are nearly as accurate as for the latter. One cause of error is the asymmetry in the rate of increase of blackening on the two sides of the null-line. This should tend to displace the settings away from the heads, but study of the question indicates that the error so introduced is unimportant. In the case of bands where the null-lines were not directly measurable, their positions were calculated from those of the corresponding heads, the necessary correction being obtained from a study of the manner in which the distance from head to null-line varies with the vibrational quantum numbers in the directly measurable cases (see next section).

Measurements on the $Si^{29}N$ and $Si^{30}N$ heads, made wherever possible, are given in Table II. Measurements on null-lines were here impossible, since these are concealed by the shading of the much more intense $Si^{28}N$ bands.

Results of Measurements on SiN Bands

Analysis of band structure. The bands consist of two branches, one starting in each direction from the null-line, the positive branch (starting toward higher frequencies) forming a head. The bands are not resolved near the null-line, nor anywhere in the positive branch; but in the negative branch, they become resolved at a moderate distance from the null-line, and can be followed for some distance (cf Plate I). It is reasonable to assume, in accord with their general appearance, that the bands are of the same type as the violet cyanogen bands, with a single missing line (the null-line) in the otherwise continuous series of lines expressible by the equation[12]

$$\nu = \nu^0 + B' \pm 2B'm + Cm^2. \qquad (1)$$

In Eq. (1) the positive and negative signs refer to the positive and negative branches, respectively; m, denoting the rotational quantum

[12] Cf A. Sommerfeld, Atombau und Spektrallinien, 4th ed., pp. 718-34.

number of the final state, is assumed to have half-integral values; for the null-line, $m=-1/2$; ν° corresponds to the change of electronic plus vibrational energy.

Measurements were made on the resolved negative branch lines of the (3,2), (4,3), (5,4), and (4,4) bands, which are at the violet end of the spectrum, where resolution is most complete. By plotting first differences of successive lines, the coefficient C was determined for each of these bands; these values of C are given in Table I. Substitution of $m=-1/2$ in Eq. (1) gives for the null-line $\nu=\nu^\circ+\frac{1}{4}C$, which is equal within experimental error to ν°, the wave-number of the band-origin,[13] since $\frac{1}{4}C$ is here negligible. For the head,[12] $\nu=\nu^\circ+B'-B'^2/C$. Letting H represent the distance from null-line to head, we then have,

$$H=B'-B'^2/C. \qquad (2)$$

The H values are obtainable from the data of Table II, and it is now possible to obtain B' for each of the four bands; the results are given in Table I.[14]

TABLE I

Experimental values of B' and C.

[Note: The data in bold-face type were determined from measurements on structure lines; the remaining data were calculated from the H data of Table II (H=distance from null-line to head) assuming B' values calculated from Eq. (3). The data are all in wave-number units.]

n'	n''	B'	$-C$	n'	n''	B'	$-C$	n'	n''	$-C$
3	2	**0.686**	**0.0303**	3	3		0.0245	4	5	0.0255
4	3	**0.685**	**0.0365**	4	4	**0.704**	**0.0305**	5	6	0.0288
5	4	**0.680**	**0.0403**	5	5		0.0336	6	7	0.0323
0	0		0.0117	6	6		0.0384	3	5	0.0152
1	1		0.0161	7	7		0.0441	4	6	0.0198
2	2		0.0199	2	3		0.0161	5	7	0.0244
				3	4		0.0210	6	8	0.0264

Now B' should be expressible in the form $B'=(h/8\pi^2J')-a'n'=B_0'-a'n'$, and $C\ (=B'-B'')$ in the form $C=C_0-a'n'+a''n''$. From the data on C for the four measured heads, preliminary values of a', a'', and C_0 can be obtained. From a' and the B' data for the four bands, a preliminary value of B_0' is then obtained, and from it and a' can be calculated the B' value for each value of n'. From these and the H

[13] Cf R. S. Mulliken, Phys. Rev. **25**, 119-138 (1925). For definition of "origin," see p. 123.

[14] B' could also be obtained by extrapolating the first difference curve (a straight line) in a suitable way to the null-line, but this method is incapable of accuracy. The values of B' and C given in Table I were, however, obtained by adjusting the curve in such a way as to give a correct extrapolation to the null-line and at the same time to agree with the measured values of H.

values obtainable from the data of Table II, a large number of C values (see Table I), corresponding to a variety of combinations of n' and n'', can be calculated; and from these, more accurate values of a', a'', and C_0 than before can be obtained. By repeating the calculation of B_0' with the new value of a', and so on, by successive approximations (one or two suffice), the following results are obtained:

$$B' = 0.728 - 0.0097\ n'; \quad C = -0.0121 - 0.0097\ n' + 0.0053 n''. \quad (3)$$

From Eq. (3) the values of B' and C, and so of H, can be calculated for *any* values of n' and n''. Values of H so obtained were used to reduce the data of Table II, in the cases where heads alone could be measured, to the corresponding values for null-lines. It should be noted that calculated values of H for this purpose could have been obtained in a purely empirical way from the measured values by studying the way in which the latter vary with n' and n''. The results would have been only slightly different, so that the subsequent analysis of the null-line data is practically independent of any possible doubts as to that of the band structure. The procedure actually used amounts to employing the theory as a means of determining the functional relation of H to n' and n'', and then using the measured values of H to determine the necessary constants so as to calculate unmeasured H values.

Dimensions of SiN molecule. From the above-determined values of B_0' and C_0, can be calculated the moment of inertia and interatomic distance of the vibrationless SiN molecule in its initial and final electronic states. From B_0' one gets $J_0' = 3.78 \times 10^{-39}$ gm cm², and $r_0' = 1.567 \times 10^{-8}$ cm. From $B_0'' (= B_0' - C_0)$ one gets $J_0'' = 3.72 \times 10^{-39}$ gm cm², and $r_0'' = 1.554 \times 10^{-8}$ cm. The values of r_0 are considerably greater, as would be expected, than for the CN molecule, where r_0 is 1.17×10^{-8} cm for what is probably the normal state.

Although the writer believes that the foregoing analysis is correct, it would obviously be desirable to study the bands under sufficient dispersion to give complete resolution in the region of the null-lines at least. Also, it may well be that the band lines, which appeared single with the dispersion used, actually consist of narrow doublets as in the violet CN bands.

Analysis of null-line data. In order to obtain an equation for the null-lines of the SiN bands, it is convenient to arrange the null-line data of Table II in a rectangular array like Table III, merely substituting them for the intensities of Table III. By an analysis of data

TABLE II

Wave-number data on S_1N bands[1]

Vibr. num. n'	n''	$Si^{28}N$ bands Head	J–M[2]	Null-line[3]	O–C[4]	Isotopic displacements[5] $Si^{29}N$ heads Rotl.[6]	Calc.[6]	Obs.[7]	$Si^{30}N$ heads Rotl.[6]	Calc.[6]	Obs.[7]
6	3	26402		26393	−5						
7	4	26135		26127	−4						
8	5	25863		25856	0						
9	6	25577		25571	−4						
2	0	26213	−1	26196	−3						
3	1	26007		25993	−2						
4	2	25787		25775	−1						
5	3	25554	3	25543	−1						
6	4	25309.7	3	25299.9	0						
7	5	25054.7	3	25045.9	0						
8	6	24790.8	3	24782.9	−1						
9	7	24518		24511	−5	$Si^{29}N$ and $Si^{30}N$ heads concealed in this region by shading of $Si^{28}N$ heads.					
1	0	25259.1	2	25234.8	2						
2	1	25080.3	2	25060.5	0						
3	2	24886.5	3	**24870.3**	0						
4	3	24678.4	3	**24664.8**	1						
5	4	24457.0	2	**24444.8**	0						
6	5	24223.9	3	24213.0	−1						
7	6	23981.8	3	23972.1	−1						
8	7	23731.4	4	23722.7	−1						
9	8	23473	−7	23465	−3						
10	9	23212		23205	−4						
0	0	24280.6	3	**24234.5**	0	−0.5	−0.5	....	−1.0	−1.0	.....
1	1	24127.8	2	**24095.0**	0	−0.4	+0.5	....	−0.7	+1.0	.....
2	2	23960.4	2	**23934.5**	−1	−0.2	1.7	....	−0.5	3.2	.....
3	3	23778.3	2	**23757.7**	0	−0.2	3.0	3.1	−0.4	5.7	5.5
4	4	23581.7	2	**23564.6**	0	−0.2	4.4	4.5	−0.3	8.4	8.8
5	5	23372.9	2	**23358.5**	0	−0.1	6.0	5.4	−0.2	11.2	11.2
6	6	23152.9	2	**23140.6**	0	−0.1	7.6	6.9	−0.1	14.3	15.1?
7	7	22924.1	3	**22913.6**	0	−0.1	9.2	10.0	−0.1	17.3	18.7
8	8	Masked by or fused with 3,4 head									

[1] For intensity data, see Table III. For the isotope heads, the intensities are all very low (0to 000(, as can be seen from Plate I.

[2] J–M = excess of Jevons' measured wave-number over the writer's. Blanks in this column represent bands not measured by Jevons.

[3] The values in bold-face type were measured directly. The other values were calculated from the data on the heads with the help of Eqs. (2) and (3): see discussion in paragraph following Eq. (3).

[4] O–C = Observed minus calculated. The calculated values are from Eq. (4).

[5] Isotopic displacement = wave-number of $Si^{29}N$ or $Si^{30}N$ head minus that of corresponding $Si^{28}N$ head.

[6] The calculated isotopic displacement for any head consists of two parts, a small (negative) *rotational* contribution (for method of calculation see second paragraph under "Confirmation of the isotope effect") and a larger *vibrational* contribution (see third paragraph under "Confirmation of isotope effect"). The "calc." (calculated) displacement is the sum of these two contributions, of which only the former is given explicitly in the table.

[7] The deficiency of observed data in the low-frequency part of the spectrum is in all cases attributable to insufficient intensity of the isotope heads, or, when so stated in the table, to masking by structure lines from a preceding head.

TABLE II—continued

Wave-number data on SiN bands[1]

Vibr. num. n'	n''	$Si^{28}N$ bands Head	J − M[2]	Null-line[3]	O − C[4]	Isotopic displacements[5] $Si^{29}N$ bands Rotl.[6]	Calc.[6]	Obs.[7]	$Si^{30}N$ heads Rotl.[6]	Calc.[6]	Obs.[7]
0	1	Not found									
1	2	Not found (although reported by Jevons)									
2	3	22856.6		**22824.6**	2						
3	4	22684.5	−4	**22660.6**	2	Masked by structure lines, etc., but also apparently abnormally weak.					
4	5	22499.8	0	**22480.5**	1	−0.2	10.3	9.5	−0.4	19.8	19.6
5	6	22302.4	2	**22285.7**	0	−0.1	11.7	11.2	−0.2	22.4	22.3
6	7	22094.6	2	**22080.1**	−1	−0.1	13.2	13.4	−0.2	25.1	25.7
7	8	21878.5	−2	21866.3	0	−0.1	14.7	15.5	−0.2	27.8	31.2?
8	9	21656.2	−8	21645.5	1	Masked by structure lines, etc.					
0	2	Not found									
1	3	Not found									
2	4	21772.3		21723.3	−1						
3	5	21605.6	−10	**21572.8**	0						
4	6	21431.6	−2	**21407.0**	1	−0.2	16.0	15.2	−0.4	30.9	31.6
5	7	21246.3	−2	**21226.8**	0	Present but masked by structure lines.					
6	8	21052.0	−5	**21035.3**	0	−0.1	18.6	19.1?	−0.2	35.7	37.2?
7	9	20848.8	−9	20834.7	1						
8	10	20637.5		20625.4	1						
9	11	20415		20404	−4						
4	7	20381.2		20346.5	0						
5	8	20206.0	2	20180.2	0						
6	9	20021.3		20000.9	−1						
7	10	19830.4		19813.7	0						
8	11	19631		19617	0						
9	12	19421		19409	−5						
6	10	19006		18980	−1						

TABLE III

Intensity distribution in $Si^{28}N$ bands, The intensities are estimated photographic intensities for a green-sensitive plate, and apply to each band as a whole, not to its head; for data on the heads, reference may be made to Jevons' paper.[2] The $\Delta n = 0$ sequence is indicated by the use of bold-faced type.

n'' →	0	1	2	3	4	5	6	7	8	9	10	11	12
n' 0	**5**	...	...	....	...	...	....	....	....	...	...	...	...
↓ 1	0	**4**	...	....	...	...	....	....	....	...	...	...	...
2	000	1	**6**	1	2	...	....	....	....	...	...	...	...
3	...	0−	2−	**10**	3	3	....	....	....	...	...	...	...
4	...	...	0	2	**8**	2	2	00	....	...	...	...	...
5	...	...	...	0+	2+	**5**	3	1+	00	...	...	...	...
6	...	...	...	000	0+	2	**2**	2	0+	0	0+	..	..
7	...	...	...	....	0−	0	1	**1**	1	0	0+	..	..
8	...	...	...	....	...	0−	0−	1	?	0	0	0	..
9	...	...	...	....	...	...	00	00	0	.	...	00	00
10	..	...	...	....	...	...	....	....	....	0	...	..	..

on the intervals between adjacent rows and columns, the following equation is then obtained, capable of representing all the null-lines

to within the amounts given in the "Obs.-Calc." column of Table II:

$$\nu = 24234.17 + 1016.30\, n' - 17.773\, n'^2 + 0.410\, n'^3 - 0.00487 n'^4 - 1145.00 n'' + 6.570 n''^2. \quad (4)$$

The comparatively large coefficients of the cubic and biquadratic terms in n' are unusual, but such terms are definitely needed to repsent the data. The relationship between the coefficients of the initial and final states is of a normal type. Since null-lines and origins[13] are probably practically coincident for the SiN bands (cf. discussion preceding Eq. (2)), Eq. (4) should hold equally for both.

Confirmation of the Isotope Effect

For each observed $Si^{29}N$ and $Si^{30}N$ head, comparison is made in Table II of the observed isotopic displacement[13] with that theoretically calculable. For a given band-head, the displacement should be the sum of a small rotational part corresponding to the distance from band-origin to band-head, and a larger vibrational part corresponding to the distance from system-origin to band-origin.[13] The rotational displacement must in every case be negative, since the distance H (head minus origin, cf Eq. (2)) is positive in the SiN bands, and is less for the two heavier isotopes than for the lightest isotope $Si^{28}N$ with which the other two are compared. The vibrational displacement should also be negative on the high frequency side of the system-origin, with the result that in each band the $Si^{29}N$ and $Si^{30}N$ heads are superposed on the shading from the $Si^{28}N$ head and so escape detection. On the low-frequency side of the system-origin, however, the vibrational displacement is positive, so that, as soon as the effect of the small negative rotational displacement is overcome, the isotope heads stand out clearly on the high-frequency side of the $Si^{28}N$ head, where there is usually nothing to obscure them seriously. This can be seen in the reproductions (Plate I), where most of the heads of Table I are visible.

The rotational isotopic displacement for a given band can be determined by calculating H of Eq. (2) for $Si^{28}N$ and subtracting the result from the corresponding value for $Si^{29}N$ or $Si^{30}N$. For $Si^{28}N$, the values of B' and C used in calculating H are obtained from Eq. (3); for the other isotopes, the following equations (3′) and (3″) must be used:

$Si^{29}N$: $B' = 0.7196 - 0.00953\, n'$;

$$C = -0.01196 - 0.00953\, n' + 0.00521\, n'' \quad (3')$$

$$Si^{30}N: B' = 0.7118 - 0.00938\, n';$$
$$C = -0.01183 - 0.00938\, n' + 0.00512\, n'' \qquad (3'')$$

The constant terms of (3′) and (3″) are obtained[13] by multiplying the corresponding terms of Eq. (3) by ρ^2, and the coefficients of the n' and n'' terms by multiplying the coefficients of Eq. (3) by ρ^3. In general $\rho^2 = (1/M_2 + 1/M')/(1/M_1 + 1/M')$. In the present case $M' = 14$ (the atomic weight of N), $M_1 = 28$, and M_2 is either 29 or 30. For $Si^{29}N$, the values of ρ, ρ^2, ρ^3, and ρ^4 are as follows: 0.994236, 0.988505, 0.982808, and 0.977142; for $Si^{30}N$, they are 0.988826, 0.977777, 0.966852, and 0.956026.

The vibrational isotopic displacement for any band can be obtained in a similar way, using Eq. (4) for the $Si^{28}N$ band, and subtracting the result from that obtained by Eq. (4′) or (4″) for $Si^{29}N$ or $Si^{30}N$. Eqs. (4′) and (4″) are obtained from (4) by multiplying each coefficient in the latter by a power of ρ equal to the power of n' or n'' with which the coefficient is associated, the constant term being left unchanged since no electronic isotope effect is to be expected.[13]

$$Si^{29}N: \nu^0 = 24{,}234.17 + 1010.44\, n' - 17.569\, n'^2 + 0.403\, n'^3 - 0.00476\, n'^4 - 1138.40\, n'' + 6.494 n''^2 \qquad (4')$$

$$Si^{30}N: \nu^0 = 24{,}234.17 + 1004.96\, n' - 17.394\, n'^2 + 0.396 n'^3 - 0.00466\, n'^4 - 1132.21\, n'' + 6.424 n''^2 \qquad (4'')$$

Practically, of course, equations obtained by subtracting (4) from (4′) or (4″), respectively, are convenient in the calculation of vibrational isotopic displacements.

Comparison of observed with calculated isotopic displacements in Table II shows complete agreement, within experimental error, throughout the range of n' and n'' values for which data could be obtained.[15] This thoroughgoing agreement seems the more remarkable when it is noted that each calculated isotopic displacement is the sum of a number of terms involving a variety of powers of ρ.[16] But such a detailed

[15] The apparent slight increase of the observed displacements relative to the calculated, as n' is increased, may be real but is within experimental error; note especially that the largest discrepancies are in the cases of the (7,7), (7,8) and (6,8) heads, which were the three weakest heads that were measurable. Also, the calculated displacements may be slightly in error due to inaccuracy in the coefficients of Eq. (4).

[16] The calculated values are considerably larger (especially for larger values of n, where the higher power terms in n have their greatest effect) than they would be if calculated according to the approximate relation[13] (which would be exact if there were no higher power terms) $(\nu_2'^n - \nu_1'^n) = (\rho - 1)\nu_1'^n$, $\nu_1'^n$ being the vibrational part of the emitted frequency for $Si^{28}N$ (equal to wave-number for given band-origin minus that for system-origin). For example, the correct calculated vibrational displacement for the (7,7) band of $Si^{30}N$ is 17.40, whereas the value obtained by the above approximate relation is $(22914 - 24235)(-0.011174) = +14.76$.

agreement, if any at all, is to be expected, since the theory is of such a nature that its detailed predictions in regard to the various coefficients all stand or fall together.[17]

The agreement of the observed with the calculated isotope effect is evidence against the possibility that half-integral quantum numbers ($\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$ . . . .) should have been employed instead of the integral numbers (0, 1, 2, ...) actually used in the calculation. If half-integral numbers were applicable, all the calculated values of Table II should be increased to approximately the mean of the given value and the value for the band having values of n' and n'' both one unit greater; this increase amounts to about 0.8 units for $Si^{29}N$ and 1.4 units for $Si^{30}N$. As a matter of fact, however, there are distinct indications[15] that there may be an effect of this sort masked by a small constant displacement in the other direction. The mean value of the observed minus calculated isotope effect is -0.1 for $Si^{29}N$ and $+0.4$ for $Si^{30}N$ (giving half weight to observed data marked doubtful, and omitting the value 31.2 for the 7,8 band). Adding 0.9 to all observed values would bring these averages to 0.8 and 1.3, respectively, which are very near the amounts 0.8 and 1.4 above calculated. Such a relative displacement in the measured, as compared with the true, interval between a $Si^{29}N$ or $Si^{30}N$ head and a corresponding $Si^{28}N$ head is not inconceivable, in view of the enormous difference of intensity. Hence the question of half vibrational quantum numbers for SiN cannot be considered definitely settled in the negative. It should be further noted that the existence of integral quantum numbers here would be in contradiction to the probable close analogy of SiN to BO for which the evidence[9] is strongly in favor of the half-integral numbers.

The evidence of the isotope effect in favor of SiN as emitter of the present bands is more definite. The only compounds other than SiN whose theoretical isotopic displacements are at all near those observed are SiC and SiO. The former need not be considered; for the latter, the value of $(\rho-1)$ is -0.00629 for $Si^{29}O$ and -0.01220 for $Si^{30}O$. These are about 9 percent greater than the corresponding values for SiN; and the same is true for (ρ^2-1), (ρ^3-1), etc., since, approximately,

[17] Although, of course, the observed agreement does not constitute a quantitative confirmation of theory for the small higher power terms, it does involve a close agreement for the linear and at least approximate agreement for the quadratic terms. An attempt to obtain equations for the $Si^{29}N$ and $Si^{30}N$ heads directly from the experimental data (such a method was used in the case of $B^{10}O$ and $B^{11}O$) in order to compare the coefficients with those of Eq. (4) for $Si^{28}N$, would not have been of much value here, on account of the fewness of the data on the isotope heads.

$(\rho^2-1)=2(\rho-1)$, $(\rho^3-1)=3(\rho-1)$, etc. Hence, every term in (and so the total magnitude of) any calculated isotopic displacement, must be about 9 percent greater for SiO than for SiN. If one adds 9 percent to each of the calculated displacements of Table II, it is apparent that the agreement with the observed displacements becomes much poorer than at present.[18] This evidence in favor of SiN is strongly supported by the chemical evidence previously cited. The fact that the known SiO bands[10] are not obtained with the present bands and have no coefficients in common with those of the latter also supports the case against SiO as a possible emitter of the present bands.

Intensity Distribution in the SiN Bands

Rotational distribution. The reproductions show strikingly, especially for the bands belonging to the sequence for which $\Delta n=0$, the rise in intensity in each branch from the null-line. In the negative branch, the intensity can be seen to rise rather rapidly to a maximum and then to fall slowly; in fact, irradiation at the end of the image of the slit on the plate has traced for each band a sort of flattened intensity distribution curve resembling that for a Maxwellian distribution. A similar rise to a maximum in the positive branch, followed by a fall before the head is reached, can be seen in the (0,0) and less clearly in the (1,1) band. Of course the apparent intensity distribution is greatly affected, especially in the positive branch, where also there is the overlap of lines returning from the head, by the changing spacing of the lines. A very rough estimate of the position of the most intense line in each branch, after attempting to discount the above effects, gives $m_{max}=13$. For thermal equilibrium, this would correspond by the equation $T=(1.431)(2B)m^2_{max}$ to a temperature of 80°C, a reasonable figure for the actual temperature, and similar to the result obtained by Birge in the case of the CN bands generated in active nitrogen.[3]

Vibrational distribution. As in the cases of BO and CN, the low effective temperature indicated by the rotational quantum number distribution is belied by the vibrational energy distribution. Instead of the very rapid fall of intensity from intense bands with $n'=0$ to very weak bands with $n'=1$ and undetectable intensity for higher n' values, the summed emission intensity actually rises from $n'=0$ until $n'=3$, and then falls gradually (cf Fig. 1). This type of phenomenon

[18] It should be noted that the effect of substituting half-quantum numbers, and that of substituting SiO for SiN, *both* would produce an *increase* of the calculated isotopic displacements, so that there is no possibility of a mutual cancellation of the two effects.

has been discussed in previous papers[19,20] on BO and on CuI, to which reference should be made.

The intensity distribution with respect to observed values of Δn appears to be very similar to that in the violet CN bands,[21] and of a type indicating, according to Lenz's theory, that the motion of the excited electron is unusually little affected by the vibration of the molecule. The sequence $\Delta n = 0$ is by far the most intense, ± 1 are fairly strong, while $+2$, -2, $+3$, -3, and $+4$ (the last represented only by one weak head, which may be spurious) follow in diminishing order of intensity. In spite of the restricted range of Δn values as compared with cases such as BO and CuI, two relations found to hold for the latter[19,20] are also clearly present in the SiN bands. These are a preference for positive over negative Δn values, and a tendency, also noted in several additional cases by Birge,[20] for the numerically larger Δn values to be associated with the larger values of n'. The general preponderance of intensity in Table III on the positive side of the diagonal drawn through the members of the sequence $\Delta n = 0$, shows the existence of the first relation. The second is shown by the increasing length of the *rows* of figures in Table III as n' increases; particular attention may be called to the low intensity of the bands (1,0), (2,0), and (0,1), (1,2), (0,2), (1,3), the last four not having been found at all.[22] An explanation of these effects in terms of Lenz's theory has been given in the paper on CuI.[20]

New System of Bands in the Silicon Nitride Spectrum

In addition to the intense system of SiN bands discussed above, which for convenience will in the following be called the A bands of SiN, a number of additional, but very much weaker bands, are

[19] See ref. 9, p. 292-3, (BO).

[20] See ref. 8, pp. 20-24, (CuI); also abstract of paper by R. T. Birge, Phys. Rev. **25**, 240 (1925), in regard to n' and Δn distribution.

[21] The resemblance is well brought out when the CN bands are obtained by the action of active nitrogen on carbon compounds. In the violet CN bands, the dominance of the sequence $\Delta n = 0$ and the tendency toward the restriction of Δn to small values are much as in the SiN bands, but perhaps somewhat less marked. Although the violet CN bands are shaded toward the violet, not toward the red like the SiN bands, this difference is a superficial one from the theoretical standpoint, being due to the fact that the coefficient C has small positive values in the first case and small negative values in the second case.

[22] This is partly due to the weakness of the *heads* of these bands, due to their large (calculated) distance from the null-lines in this region. But if the bands had been at all intense, the region of maximum intensity on either side of the null-line would certainly have been seen.

TABLE IV

Wave-number data on heads of new bands.

Heads marked "masked" are concealed usually by bands of the more intense SiN system. Heads marked * appear only as emphasized structure lines of a SiN or NO band; in the case of those marked †, two heads fall together; those marked ? are of doubtful identity as members of the system.

Wave-numbers for $n'=7$, $n''=0$ should be added to the Table. They are 31372 and 31348.

$n'\rightarrow$	0	1	2	3	4	5	6
n'' 0	.....	.....	28050* *678*	28728 *673*	29401 *664*	30065 *657*	30722 *650*
↓	.....	.....	28017* *682*	28699 *674*	29373 *665*	30038 *659*	30697 *651*
			1019	*1018*	*1021*	*1022*	*1020*
			1012	*1017*	*1019*	*1020*	*1027*
1	.....	26348† *683*	27031 *679*	27710 *670*	28380 *663*	29043 *659*	29702*
	.....	26318 *687*	27005 *677*	27682 *672*	28354 *664*	29018 *652*	29670*
		1005	*1008*	*1009*	*1009*	*1008*	
			1004	*1010*	*1010*	*1014*	
2	.....	25343 *680*	26023 *678*	26701 *670*	27371 *664*	28035*	
	.....	Masked	26001* *671*	26672 *672*	27344 *660*	28004*	
		1001	*997*		*998*		
					996		.....
3	.....	24342 *684*	25026	Absent	26373	.....	.....
	.....	24318	Absent	Absent	26348*	.....	.....
					979		
					978		
4	Masked	.....	.....	Absent?	25394	.....	.....
	22649	.....	.....	Absent	25370	.....	.....
	970						
5	21708 *691*	22397 *689*	23086	Masked	.....	.....	.....
	21679 *691*	22370 *688*	23058 *681*	23739?	.....	.....	.....
		958					
		957					
6	.....	21439	Absent or	22802 *668*	23470*	.....	.....
	.....	21412	Masked	Masked	23438*		
		943		*937*	*943*		
		943					
7	19804 *692*	20496 *685*	21181 *684*	21865? *662*	22527	Absent or	.....
	19784 *685*	20469 *685*	21154 *679*	21833?	Masked	Masked	
	931	*934*	*933*	*938*			
	935	*930*	*936*	*938*			
8	18873† *689*	19562 *686*	20248 *679*	20927	Absent or	.....	.....
	18849† *690*	19539 *679*	20218 *677*	20895	Masked	.....	.....
		923	*921*				
		931	*915*	*913*			
9	.....	18639? *688*	19327		20678	.....	.....
	.....	18608* *?695*	19303 *679*	19982 *674*	20656	.....	.....
			911		*910*		
			912	*910*			
10	.....	.....	18416 *681*	19097 *671*	19768	.....	.....
	.....	.....	18931* *681*	19072	.....	.....	.....
				894	*895*		
				895			
11	.....	.....	.....	18203 *670*	18873†	.....	.....
	.....	.....	.....	18177 *672*	18849†	.....	.....
					877		
					880		
12	.....	.....	.....	.....	17996	.....	.....
	.....	.....	.....	.....	17969	.....	.....
					[*866*]		
					[*864*]		
13	.....	.....	.....	.....	.....	[*663*]17793	.....
	.....	.....	.....	.....	.....	[*663*]17768	.....

present. Their presence is obvious only in the near ultraviolet and in the green, but on careful examination it was found that they extend through the intervening region and belong to a single system. They are all shaded toward the red, and in the ultraviolet, where conditions are most favorable, are seen to become resolved, at a moderate distance from the head, into a series of structure lines. The heads are in pairs of about equal intensity, with a separation averaging 26.8 wave-number units and apparently constant or nearly so.

Measurements, of no great accuracy, were made on the heads of the new bands in the hope of finding possible relations between them and the A bands. The wave-number data are given in Table IV, and the intensities in Table V. The former are so arranged as to show the

TABLE V

Intensity distribution in new bands (estimated photographic intensities). Vacant spaces represent bands not found; a few of these may be weakly present but masked by heads of the more intense SiN system.

$n''\rightarrow$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
n' 0	...	...	...	...	00	0	...	0−	0+	...	...	...	...	...
↓ 1	...	0−	0	0−	...	1	0+	1	0−	0+?	...	...	...	...
2	00	1−	1−	(2)	...	0	...	0+	1	2+	0	...	...	...
3	0−	1	1	...	...	0?	0+	0?	0	0	1+	1	...	...
4	1−	2−	0	0−	0	...	1−	0	...	1	00	0+	1	...
5	0	0	00	...	...	...	...	...	...	...	...	...	...	0
6	0−	000	...	...	...	...	...	...	...	...	...	...	...	...
7	00	...	...	...	...	...	...	...	...	...	...	...	...	...

constant differences between adjacent rows and columns which is the basis of the assignment of vibrational quantum numbers made. On account of the peculiar intensity distribution, the absolute numbering is somewhat uncertain in respect to n', but is quite definite in regard to n'', since there is no indication of additional bands in the ultraviolet beyond the relatively intense series for which $n''=0$. The positions of the heads of the new bands can be represented approximately (a systematic analysis to determine the best values of the coefficients has not been made) by the equation:

$$\nu=\left\{\begin{matrix}26676\\26649\end{matrix}\right\}+694n'-3.3n'^2-1025.9n''+6.4n''^2. \qquad (5)$$

From a comparison of Eqs. (4) and (5) it is evident that the new bands have no term in common with the A bands. Although the new bands are presumably due to SiN, there is no definite proof of this from the isotope effect; but this could not have been expected, on account of the low intensity of the bands even in the most intense exposures.

Observations on the new bands showed them to be quenched in the same manner as the A bands by small amounts of oxygen. This indicates that they are due to the same emitter. Also, the numerical values of the coefficients and the spacing of the structure lines are of the same order of magnitude as for the A bands. It is possible, of course, that the new bands are not due to SiN, but to some other diatomic emitter such as Si_2 or SiP. SiCl must be ruled out, since the relative abundance of the isotopes of chlorine is such that both $SiCl^{35}$ and $SiCl^{37}$ heads should have been visible even with the low intensities used.[23]

TABLE VI

Unidentified heads or lines in SiN spectrum.

Wave-No.	Type	Int.	Wave-No.	Type	Int.	Wave-No.	Type	Int.
24267		1	22777	v	3−	21088		1d
149	l?	0	745	v	3−	071		1d
23989	l?	3	446	v?	0	20816	l?	0
960		0	423	v?	0+	773	r	0−d
871	l	0+	016	v	1+	736	r	0−d
836	l	1+	21970	l?	*0+	146	v?	00
712		0	963	l?	*0+	142	v?	00
232	l?	1+	925	v?	1−	19993	r	00
176	l?	1	914	v?	0+			
22997	l?	3	822	v?	1			
985	l?	3−	818		0			
970	v?	2+	800	v?	1			
949	v?	1	797		0			
894	v	3	715	l?	1−			
870	v	3	291	v?				

Notes: l = line; v = shaded toward violet; r = shaded toward red; d = diffuse; * means superposed on structure line.

The intensity distribution (cf Table V) in the new bands is of an interesting type characterized by a preference for numerically large Δn values, and by the non-occurrence of the band (0→0) and neighboring bands. This distribution approaches that typified by the visible iodine bands.[24] It indicates that the motion of the emitting electron is very markedly affected by the vibration of the molecule.—It should be stated that Tables IV and V include all bands of appreciable intensity, except possibly at the extreme red end.

From the analogy of SiN to CN one might expect in the red or near infrared a system of SiN bands analogous to the red CN bands. No such bands were found, presumably because they lie too far in the infrared. Possibly the new SiN system has for its final electronic state a doublet state identical with the initial state of the hypothetical red SiN bands. In

[23] Also, these bands have not been reported by Jevons (Proc. Roy. Soc. **106A**, 174, 1924) in his investigation of the discharge through pure $SiCl_4$ vapor.

[24] Cf refs. 12 and Birge, ref. 20; and especially R. Mecke, Phys. Zeits. **26**, 234 (1925).

addition to the new bands and the A bands, there are a number of unidentified lines or heads; the data are given in Table VI. Some of these are rather intense, and many are shaded toward the violet; it is possible that these last will prove of importance in the spectrum of SiN.

The writer wishes to express his gratitude to Prof. G. P. Baxter of the Chemistry Department for the pure $SiCl_4$ used in the above work.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
June 5, 1925

THE IONIZATION OF HCl BY ELECTRON IMPACTS

By E. F. Barker and O. S. Duffendack

Abstract

Ionization of HCl.—Current-voltage curves obtained by means of a two electrode, hot cathode discharge tube indicate ionization in stagnant HCl gas at 14 volts in agreement with the value of the ionizing potential reported by previous observers. Spectrograms showed no hydrogen lines at voltages near the ionizing potential, but they appeared faintly at higher voltages along with some bands. A considerable amount of dissociation of the gas was observed, and this was shown to be due to thermal action at the filament rather than to the discharge. The presence of dissociation products made the interpretation of the critical potential doubtful, and so the apparatus was modified to eliminate these from the region of observation. With HCl flowing continuously through a three element discharge tube in such a way that it passed through the observation chamber, where the electron impacts occurred, before it reached the filament, no hydrogen lines appeared at accelerating voltages up to 120 volts. Current-voltage curves again show a *critical potential* at 14 volts which is attributed to the ionization of the molecule without dissociation. No *band spectra* of wave-lengths between 6000 and 2000A accompany this excitation. Hence it is concluded that the molecule has no electron transitions involving a change of energy between 2 and 6 volts. When an HCl^+ ion is neutralized, the electron is probably bound in a single operation with the consequent radiation of energy equivalent to about 14 volts.

Effect of HCl on a tungsten filament.—The conductivity was observed to increase 10 percent in 5 hr. Langmuir suggests that WCl_6 formed at the cooler ends is dissociated at the hot section.

THE ionization potential of HCl has been measured by Foote and Mohler,[1] by Knipping,[2] and by Mackay.[3] These observers agree on the numerical value of the ionizing potential, but disagree in their interpretation of the process of ionization. Foote and Mohler report 14 volts and suggest that it corresponds to the dissociation of the HCl molecule into a positive hydrogen ion and a negative chlorine ion. This interpretation is based upon the fact that the work involved in the production of these ions from the molecule, which can be computed from known heats of reaction, is equivalent to 13.7 volts. Mackay reports 13.8 volts for the ionizing potential but finds no evidence of dissociation and concludes that the process involves simply the removal of one electron from the molecule. He used a modified Lenard method of

[1] Foote and Mohler, Amer. Chem. Soc. Jour. **42,** 1832 (1920).
[2] Knipping, Zeits. f. Phys. **7,** 328 (1921).
[3] Mackay, Phil. Mag. **46,** 828 (1923) and Phys. Rev. **23,** 553 (1924).

measurement[4] employing a photo-electric source of electrons and thus eliminating thermal dissociation of the molecule. We find that the latter point of view is confirmed by a spectroscopic study of the impact region when HCl is subjected to an intense electronic bombardment.

METHOD

In the early experiments of this investigation, HCl was generated by dropping concentrated H_2SO_4 on pure NH_4Cl, dried by passing over P_2O_5 and admitted at pressures of 0.01 to 0.2 mm into a simple two electrode discharge tube. The cathode was a 12 mil (0.3 mm) tungsten spiral, and the anode a platinum plate. The minimum voltages at which an arc could be struck and maintained were determined under varying conditions of pressure and filament temperature. As ionization is essential for the striking and maintaining of an arc, this minimum voltage is the ionizing potential of the gas unless ionization by cumulative action occurs, and it apparently did not occur in our experiments. The results obtained are in agreement with the value of the ionizing potential reported by the previous observers. Spectrograms were taken of these arcs in HCl with glass and quartz spectrographs, and these were examined especially for the Balmer lines of hydrogen which should appear if H^+ ions are found in any appreciable concentration in the region of the arc or if hydrogen gas is present in appreciable amount.

The appearance of $H\beta$ on the plates and the gradual accumulation of a gas not condensible at the temperature of liquid air indicated that some dissociation of the HCl had occurred. This was found to be due largely to thermal action at the filament, however. It was consequently necessary to so modify the procedure as to eliminate as far as possible the effects of these decomposition products from our observations. This was accomplished by employing an apparatus arranged as shown in Fig. 1, in which diffusion of gases from the neighborhood of the filament into the region of observation is minimized. A molybdenum diaphram, fitting the tube closely, was inserted between the filament and the plate—about 1 mm from the former and connected to the plate by a wire. This divided the tube into two compartments and separated the filament from the region of electron impacts. A fine platinum gauze covered a small aperture in the diaphram and served as a window for the passage of the gas through the tube and of electrons from the filament. A continuous flow of HCl through the observation chamber and *towards* the cathode was maintained, the rate being controlled by a

[4] Compton and Mohler, Critical Potentials, Nat. Research Coun. Bull. 48.

special stopcock *S*, with an indicator and scale. The gas passed out of the discharge tube through an arm sealed on directly above the filament and was condensed in the second liquid air trap shown in the diagram. The pump was operated continuously during a run to take off any uncondensed gas. A field for accelerating electrons was set up between the filament and the gauze, and the electrons passing through the gauze made impacts with the HCl molecules in an equipotential region between the diaphram and plate. The radiation from this region was photographed with a small Hilger quartz spectrograph through a quartz

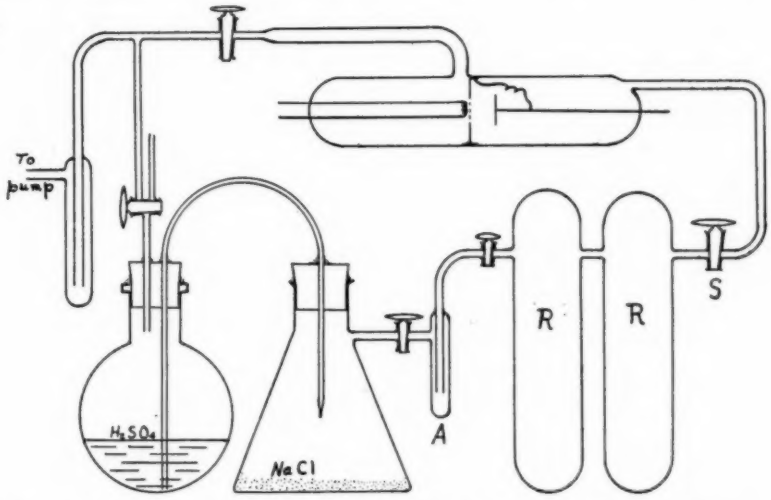


Fig. 1. Arrangement of apparatus for providing a continuous flow of HCl through the discharge tube.

window sealed on to the discharge tube, and the combined grid and plate current was measured for various accelerating voltages and gas pressures. The results indicate that the effects of dissociation at the filament and of chemical action following such dissociation were completely eliminated.

An adequate supply of HCl was prepared in advance. Concentrated H_2SO_4 and NaCl of the highest purity were introduced into the generator shown in Fig. 1 and the whole system evacuated. Then air was admitted above the H_2SO_4 in the flask causing the acid to drop slowly upon the salt. The evolved gas was collected up to atmospheric pressure in the reservoir *R*, the stopcocks closed, and the excess HCl allowed to escape through the acid flask. Liquid air was next applied to the trap *A*, condensing the HCl and any water vapor which might have

been present. The reservoir was then opened to the pump once more, and a small amount of uncondensed gas which was present was pumped off. Finally, about two-thirds of the condensed HCl was permitted to evaporate into the reservoir, the remainder being released through the generator. The gas thus collected was found to contain no detectable impurities.

Results

Typical current-voltage curves for the *stagnant gas* are shown in Fig. 2, in which the arc current is plotted against the accelerating volt-

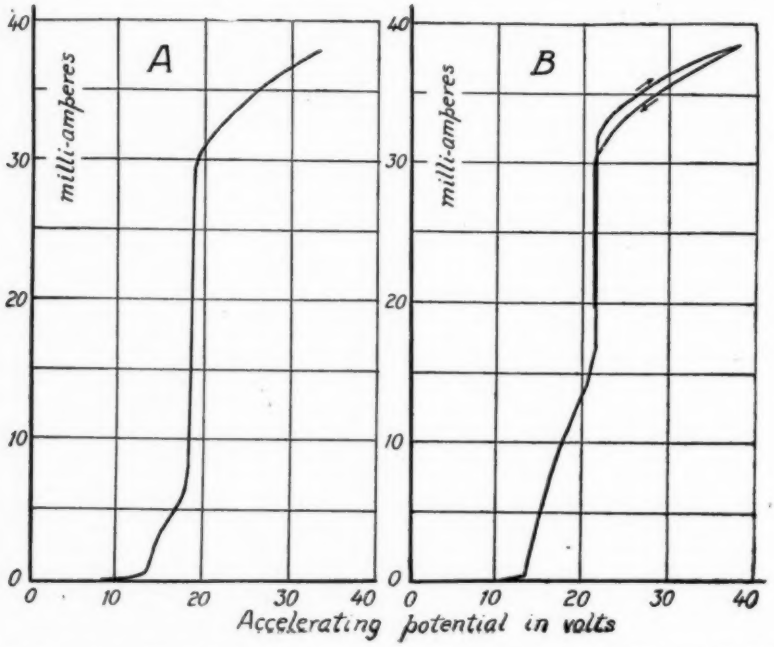


Fig. 2. Current-voltage curves in stagnant gas. The arc current in milli-amp. is plotted against the accelerating voltages. Initial pressure 0.15 mm for curve A and 0.06 mm for curve B.

age. In each an abrupt increase in current at about 14 volts is apparent, while the arc struck at somewhat higher potentials, the values of which are a function of the pressure of the gas and the temperature of the filament. The arcing potential seemed also to depend somewhat upon how long the gas had been in the tube.

The discharge was entirely colorless. At voltages above 37 the spectroscope showed Hβ faintly. Exposures of several hours at accelerating potentials up to 60 volts showed only the hydrogen lines and some

bands in the ultraviolet. These bands did not appear consistently on the plates and were probably due to accumulated reaction products, perhaps chlorine and metallic chlorides. While the tube was operating there was a noticeable clean-up of the gas, and after each run it was found that a considerable fraction of the residual gas would not condense in a liquid air trap. This must have been hydrogen, and the appearance of the Balmer lines is thus accounted for. The interpretation of the critical potential at 14 volts is in doubt, however, so long as other gases are present in the discharge tube.

Typical ionization curves obtained *with gas flowing* through the tube are shown in Figs. 3 and 4. In Fig. 3, curve *a* was obtained with no gas in the tube, and curve *b* directly afterward with a continuous flow of HCl. The arc struck at about 20 volts, but ionization set in at 14

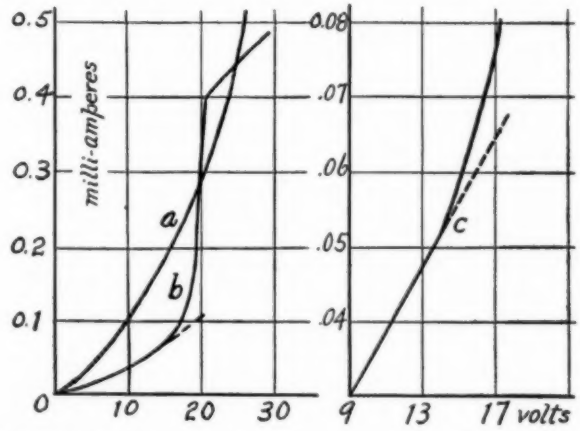


Fig. 3. Current-voltage curves. The arc current in milli-amp. is plotted against the accelerating voltages. Curve (a) without gas; (b) with HCl flowing; (c) part of curve b magnified.

volts. This is apparent from the change in curvature along a small part of this curve when plotted to a larger scale as shown in curve C. The abrupt change in slope between 13 and 14 volts is at once evident. The curve of Fig. 4 represents conditions similar to those of Fig. 3(b), and shows no other discontinuities up to 120 volts. Runs like these were made for pressures up to 0.1 mm with various filament temperatures. The average of the ionization potentials indicated is about 14 volts.

The spectrograph failed to reveal any radiation whatsoever between 6000 and 2000A when pure HCl gas flowed continuously through the apparatus. Even the Balmer lines were missing, though exposures

were made with accelerating potentials as high as 120 volts. This fact, together with the absence of deposits on the plate side of the molybdenum diaphram resulting from reactions of the gas after contact with the filament, led to the conclusion that the gauze and gas stream were effective in keeping the observation region free from impurities.

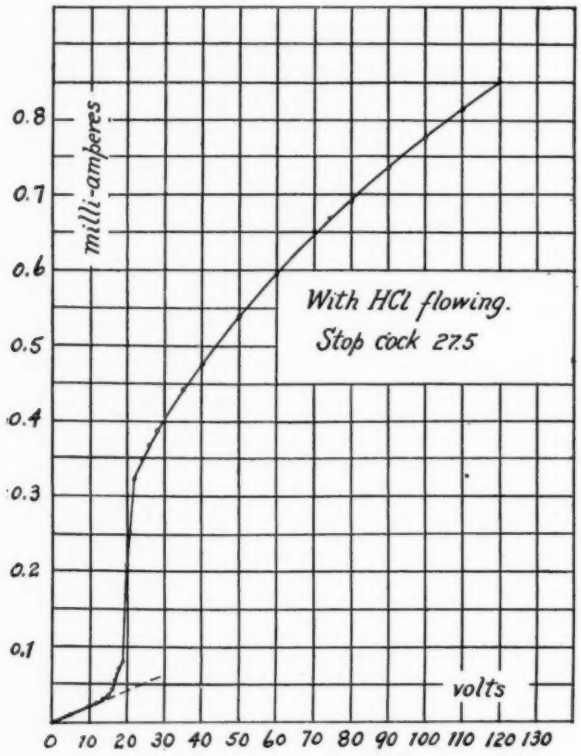


Fig. 4. Current-voltage curve for flowing gas, 0—120 volts.

The effect of the gas upon the filament is of particular interest. In Fig. 3, curves *a* and *b* were obtained with the same filament current. It will be noted that the thermionic emission for voltages below the arcing potential is very much less when gas is flowing. This is partly due to the cooling of the filament by the gas, and partly, perhaps, to a modification of the emitting surface by chemical action. The behavior of the filament in the presence of the gas was unusual in that its conductivity, instead of decreasing with use, increased throughout nearly the whole of its life. As computed from the ratio of the currents required to produce a certain potential drop across the filament, the conductivity in one instance increased over ten percent in five hours with

gas flowing at a pressure of about 0.1 mm.[5] Accompanying this action there is dissociation of the HCl, for a McLeod gauge near the mercury diffusion pump always read zero when the filament was cold and read about 0.0003 mm when the filament was hot. As the liquid air completely removed the HCl, this pressure was due to some dissociation product, undoubtedly hydrogen. The approximate rate of thermal dissociation was determined by shutting off the pump and heating the filament in stagnant gas. After 45 minutes it was found that about one-third of the gas remaining in the tube failed to condense in the liquid air trap. No increase in the amount of accumulated hydrogen was observed under similar conditions when an arc of 1.5 milli-amp. was maintained in the tube. This indicates that the amount of dissociation by electron impacts is entirely negligible compared with that produced by thermal action, and the failure of the hydrogen lines to appear supports this conclusion. The absence of dissociation in the arc implies that at the critical potential of 14 volts a molecular ion of HCl is formed.

The fact that no radiation of wave-lengths between 6000 and 2000A appears indicates that the molecule has no electron transitions involving a change of energy between 2 and 6 volts. After recapturing an electron, therefore, the normal state must be reached by a single transition, or else by combinations of steps of less than 2 and more than 6 volts. The behavior of other molecules indicates that two nearly equal steps are hardly to be expected. Also the fact that no critical potentials have been detected below that of ionization indicates the binding of the electron in a single operation with the consequent radiation of energy equivalent to about 14 volts.

PHYSICS LABORATORY,
UNIVERSITY OF MICHIGAN.
June 9, 1925.

[5] We are indebted to Dr. Langmuir of the General Electric Company for an explanation of this effect. The cooler parts of the filament are attacked by atomic chlorine from the dissociated HCl, WCl_6 being formed. This compound has a considerable vapor pressure at the temperature of the tube. The vapor is decomposed at the hot section of the filament, and metallic tungsten deposited there. The central part of the filament assumed a granular appearance after being heated in the gas due to this crystalline layer. Cf Langmuir, Amer. Chem. Soc. Jour. **37**, 1162 (1915).

CRITICAL POTENTIALS IN SECONDARY ELECTRON EMISSION FROM IRON, NICKEL, AND MOLYBDENUM

By Robert L. Petry

Abstract

Secondary electron emission from iron, nickel and molybdenum targets for primary voltages 0 to 1500.—The tube used was designed so as to minimize disturbing factors, all metal parts were glowed before assembly, and the tube was baked before each set of runs. In addition the targets were thoroughly cleaned by heating to bright red by electronic bombardment from an auxiliary filament until a permanent condition was obtained as indicated by the curves. The pressure was kept below 10^{-6} mm. Both the secondary emission I_1 and the primary current I_2 were measured by a null method of high precision (to 0.1 percent or less). The ratio I_1/I_2 was found (1) to vary only 2 percent as the retarding potential between the plate and surrounding box was increased from 3 to 10 volts, so 6 volts was considered sufficient; (2) to vary only slightly with the primary current; (3) to be unchanged when the earth's magnetic field was neutralized. The final curves, for all three metals after heat treatment, are nearly alike, the value of I_1/I_2 rising to a maximum of about 1.30 at about 348 volts for iron, 455 volts for nickel and 356 volts for molybdenum. From slight breaks (changes of slope) in the curves, some 25 critical potentials were located for iron, 16 for nickel and 20 for molybdenum. The values below 40 volts for iron (7.3, 11.6, 14.4, 18.3, 22.6, 25.0 and 29.0) and for nickel (6.2, 9.3, 9.9, 11.8, 15.1, 22.6, 24.4, 31.4, 35.0) agree fairly well with critical potentials for soft x-rays determined by Thomas. This suggests that there is a common phenomenon involved in the production of secondary emission and of soft x-rays which is evident at the lower voltages but which is masked at higher voltages by other processes not yet understood.

Introduction

IT HAS been known for some time that when electrons strike a metal surface in a vacuum they cause the emission of secondary electrons from the metal. The work of the earlier investigators[1–10] in this field

[1] A. Gehrts, Ann. der Phys. **36**, 995 (1911).
[2] N. Campbell, Phil. Mag. **22**, 276 (1911); **25**, 803 (1913); **28**, 286 (1914); and **29**, 369 (1915).
[3] A. W. Hull, Phys. Rev. **7**, 1 and 141 (1916).
[4] H. M. Dadourian, Phys. Rev. **14**, 434 (1919).
[5] J. T. Tate, Phys. Rev. **17**, 394 (1921).
[6] Davisson and Kunsman, Science **54**, 394 (1921).
[7] I. G. Barber, Phys. Rev. **17**, 332 and 292 (1921).
[8] L. E. McAllister, Phys. Rev. **21**, 122 (1923).
[9] Horton and Davies, Proc. Roy. Soc. **97A**, 23 (1920); Phil. Mag. **46**, 129 (1923).
[10] E. W. B. Gill, Phil. Mag. **45**, 864 (1923).

has shown that (1) the number of secondary electrons emitted depends on the nature of the metal and is a function of the velocity with which the primary electrons strike, (2) the number of secondary electrons, at the higher voltages, may exceed the number of primary electrons striking, so that reflection alone is not sufficient to account for the phenomenon, and (3) the emission is dependent upon the previous heat treatment of the metal bombarded. Recently Farnsworth[11] has made a careful study of the ratio of secondary emission to primary current for various metals after careful heat treatment and has investigated the effect of heat treatment of copper upon its emission. Stuhlman[12] observed, in the case of iron, that the relation between the number of secondary electrons per primary electron and the velocity of the primary electrons changes more or less abruptly at certain values of velocity, thus indicating critical velocities (or voltages) for secondary emission.

The object of the present investigation has been to determine more exactly whether the number of secondary electrons emitted per primary electron changes gradually as the velocity of the primaries is increased, or whether at certain critical velocities this number changes abruptly. It was assumed that a considerable part of the secondary emission, if not all of it, might be due to the photo-electric action of soft x-radiation which is caused by the electronic bombardment of the metal surface and which acts photo-electrically on the metal itself in which it originates; if this is the case, a relation or correspondence should be found between these critical velocities for secondary emission and those for x-ray emission.

Apparatus and Procedure

The apparatus used was of the same form as that used by Campbell[2] and A. W. Hull.[3] Electrons from a filament F_1 (Fig. 1) were drawn toward a series of diaphrams with openings *SSS* by a field V_1, and all those passing through the openings struck a metal plate *P*. Any electrons reflected from *P* or emitted as secondary electrons were drawn by a field V_2 to a nickel cylinder *CC* almost completely surrounding *P*. The current to *CC* was measured by a galvanometer G_1, and the total current through *SSS* by a second galvanometer G_2.

The plate *P* was mounted through a ground glass joint sealed on the outside with DeKhotinsky cement, so that it could be replaced or

[11] H. E. Farnsworth, Phys. Rev. **20**, 358 (1922) and **25**, 41 (1925); Proc. Nat. Acad. Sci. **8**, 251 (1922).

[12] Stuhlman, Science, **56**, 344 (1922); Phys. Rev. **25**, 234 (1925).

taken out for polishing without cutting the tube. The ground glass joint was long and was kept free from cement except at the outside, where it was kept cool by water circulation; consequently the cement vapor pressure was small because of the difficulty of diffusion between the ground glass surfaces and because of rapid evacuation by the pumping system. The filament F_1 was mounted similarly through another ground glass joint.

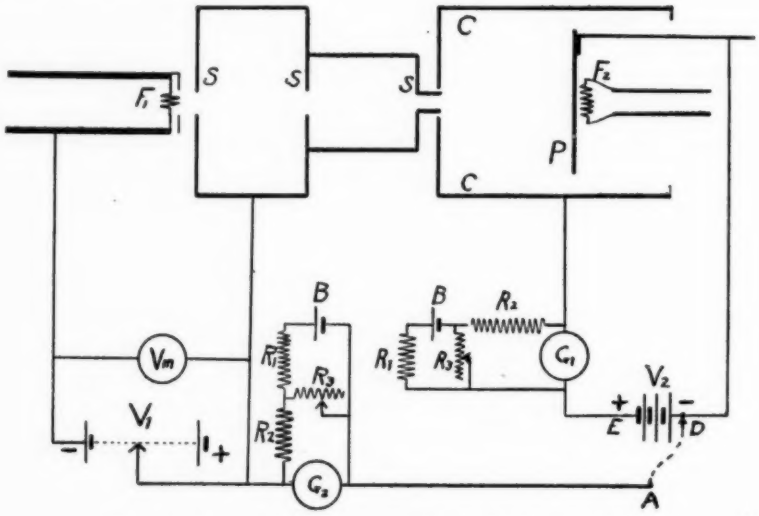


Fig. 1. Diagram of apparatus and electrical connections.

The filament F_1 was of 10 mil (.25 mm) tungsten wire helically wound in three closely-spaced turns of small diameter so as to give a small, nearly equipotential source of electrons. The heating current required varied from 5.8 to 6.3 amp., with a potential drop of 1.1 to 1.2 volts. This current was supplied by a large capacity insulated storage battery, which was used under conditions suitable for giving the greatest possible constancy of the current. A rheostat consisting of a nichrome ribbon immersed in kerosene, with heavy clamp contacts, was found to furnish a very steady control resistance. A focusing ring of nickel sheet was mounted a short distance in front of the filament but the potential applied to it was found to have little effect upon the amount of current passing through the openings, and in most of the runs it was left connected to the negative filament terminal.

The system of three diaphrams *SSS* and the cylinder *CC* were of nickel and both were mounted directly against the walls of the glass tube which was of 3.5 cm diameter. These two parts were so designed

as to give about an inch of glass insulation between them. The diaphrams were spaced 1.5 cm apart and the openings were circular holds 2.5 mm in diameter. The distance from the filament F_1 to the plate P was 5 cm.

All metal parts were glowed out in an induction furnace before being assembled, in order to remove occluded gases. Before each set of runs all parts of the tube, with the exception of the water cooled DeKhotinsky seals and two charcoal traps in series with it, were baked out for several hours in electric furnaces at a temperature of about 400°C. Liquid air was kept on a third trap continuously in order to keep mercury and oil vapors from entering the tube. A second filament F_2 was mounted directly back of the plate P, and after the tube was allowed to cool the plate was glowed out several times at a bright red heat by electronic bombardment from F_2 in order to remove occluded gases from the surface to be bombarded. The temperature used in this process was sufficient to cause the iron target to show signs of melting at the point nearest the filament. As a result of these precautions, with the diffusion pump running continuously and liquid air on both charcoal traps, during runs the pressure was too small to be detected by a McLeod gauge reading to $(10)^{-6}$ mm of mercury.

The accelerating potential V_1 was varied from 0 to 1500 volts. Storage cells were used up to 300 volts, while for higher ranges a motor-generator set run by storage batteries was used. V_1 was adjusted by a 12,000 ohm potentiometer system and was measured by a Weston Laboratory Standard Voltmeter with a scale of 750 divisions and with suitable multiplying resistances to give convenient ranges.

The retarding potential V_2 was usually about 6 volts and was furnished by dry cells. Part of the runs were taken with the connections shown but most of the later ones were taken with A (Fig. 1) connected to E instead of to D, so that the strong field in the close gap between the projecting tube of SSS and the edge of the hole in the end of CC was avoided. The accelerating field from F_1 to P was then $V_1 - V_2$. The results from the two methods of connecting were indistinguishable.

It will be noted that the current reflected directly back through the opening in the end of CC was lost. This could cause the observed ratio of secondary electrons to primary electrons to be smaller than the actual ratio. However, the solid angle subtended at P by the opening was not more than 2.5 percent of the entire solid angle and the loss was assumed to be negligible. In any case this source of error should not affect the location of critical potentials.

Multiple reflection and emission from CC back to P have also been neglected. However, velocity distribution measurements by Farnsworth and the writer indicate that a collecting potential V_2 of 6 volts should be sufficient to avoid any considerable final reflection or emission from CC to P since a large proportion of the secondary electrons have velocities insufficient to carry them against this collecting field.

The current to CC was usually of the order of $(10)^{-6}$ amp. and was measured by a galvanometer G_1 of sensitivity better than $(10)^{-9}$ amp. per scale division. In order to measure the total current coming through SSS and striking P the second galvanometer G_2 was connected so as to measure the current to both P and CC; that is, the electrons remaining on P plus those reflected or emitted from it to CC. The filament current was adjusted so that, except at the lowest voltages, this current through G_2 was greater than $(10)^{-6}$ amp., while the sensitivity of G_2 was about 5 $(10)^{-9}$ amp. per scale division.

In order to obtain greater precision the galvanometers were not shunted in measuring the larger currents, but were used at full sensitivity for all ranges by a method of balancing currents, in which the galvanometer measured only the residual current after approximate balancing by the following potentiometer method. Whenever the scale reading of one of the galvanometers became large it was reduced to near zero by sending an additional current through the galvanometer in the reverse direction by means of a storage cell B connected through two high resistances R_1 and R_2 and a shunt R_3 of low variable resistance. In this way the major part of the current to be measured was balanced by an accurately known reverse current, while the galvanometer, at full sensitivity, measured the difference between these two. As the currents increased, during a run, it was necessary to change this balancing current at intervals; the correction factor to be added at each step-down of this kind in the scale reading was not computed but was observed directly for each change of R_3 by noting the difference between readings taken before and after changing R_3, all other factors remaining constant. A reliable check on the steadiness of conditions during this change for one galvanometer was given by observations on the readings of the other galvanometer. Below 50 volts the currents were generally satisfactorily steady but above that range there were generally slow and regular drifts of both currents in the same ratio; under these conditions duplicate readings were taken on changing R_3 in order to determine the correction satisfactorily. The largest current

measured in this way was the equivalent of about 4000 scale divisions of the galvanometer used.

The ratio of the current through G_1 to the current through G_2 gives the number of secondary electrons emitted from the target per electron striking it. This ratio I_1/I_2 was plotted as ordinate against V_1 (or $V_1 - V_2$ with changed connections) in volts as abscissa. The resulting curves showed breaks or places of rapid change of slope. In order to locate these accurately, readings were taken at small voltage intervals. In the region 0 to 24 volts the intervals were 0.2 volts; in the region 650 to 1500 volts, 10-volt intervals were used, while intermediate intervals were used in the intermediate regions. The correction in the value of V_1 for initial velocity of the electrons was estimated at 0.2 volts and for potential drop to the middle of the filament was 0.55 volts; but the correction for contact difference of potential is not known accurately. Hence, the total correction due to these causes was checked experimentally for iron and nickel by observing the retarding potential $-V_2$ with A connected to E, which was necessary to keep the majority of electrons from reaching P under an accelerating field V_1. This correction was -0.4 volts for iron and $+0.8$ volts for nickel.

The present investigation differs from other studies made in the same field in the smaller voltage intervals used in taking readings and in the precautions taken to measure the currents and the accelerating voltage precisely while avoiding disturbing factors.

Results

Preliminary observations were made to determine the effect upon the ratio of secondary emission to primary current of four factors, viz., variation of collecting potential V_2, variation of filament current, compensation of the earth's magnetic field, and heat treatment of the target.

An increase of V_2 from 3 to 10 volts increased the ratio I_1/I_2 by about 2 percent in most cases. Increasing V_2 from 6 to 20 volts had a smaller effect. In general so long as V_2 was not negative it had little effect upon the ratio I_1/I_2 and none at all upon the position of breaks in the graph of I_1/I_2 plotted against V_1.

Results taken with different filament currents were as consistent as regards critical potentials as were runs taken with the same filament current, hence various filament currents were used throughout and the results were plotted without regard to this factor. In general, however, with an increase of filament current the ratio I_1/I_2 showed a tendency

to decrease slightly; this shows that not the absolute values of the ratio but its relative values for any one run were determined precisely.

A few runs were taken with two long bar magnets placed so as to compensate the earth's magnetic field approximately over the path of the primary electrons. No difference could be distinguished between the results of these runs and the results of runs taken without the magnets. The nickel parts of the apparatus may have provided considerable magnetic shielding for the electron paths.

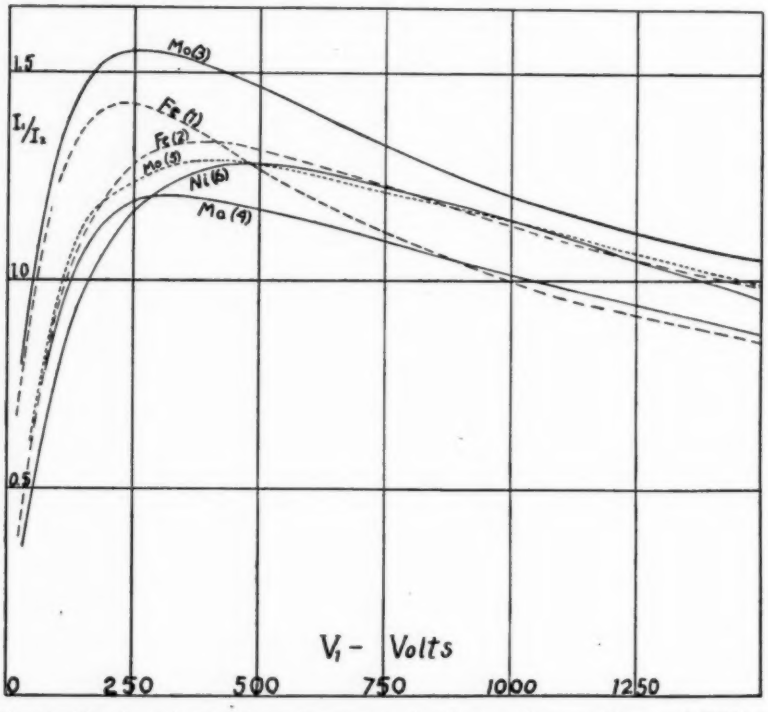


Fig. 2. Number of secondary electrons emitted per primary electron, 0-1500 volts.
Curves 1 and 2, Fe before and after heat treatment.
Curves 3 and 4, Mo before and after partial heat treatment.
Curve 5, Mo in final state.
Curve 6, Ni after heat treatment.

The effect of previous heat treatment of the target was not investigated at length. In general this reduced the ratio I_1/I_2 and the curves approached a limiting form in agreement with results found by Farnsworth. A maximum in the ratio was found at about 225 volts for iron and at about 275 volts for molybdenum before glowing out the target by electronic bombardment (curves 1 and 3, Fig. 2); similar maxima

in the same general region, 200 to 275 volts, were reported by Gehrts[1] for copper, aluminium and cobalt targets not glowed out in vacuo. But it was found that after thorough heat treatment this maximum came permanently at 356 volts for molybdenum and at 348 volts for iron (curves 2 and 3, Fig. 4).

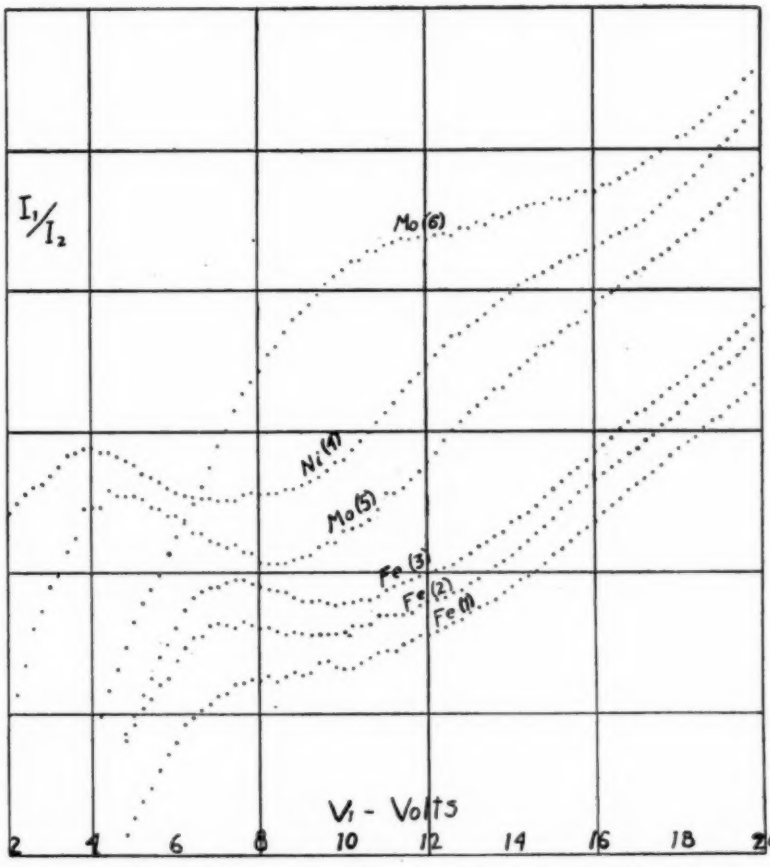


Fig. 3. Secondary emission curves, 2-20 volts. Different scales of I_1/I_2 are used.
Curves 1, 2, and 3, Fe, after thorough heat treatment.
Curve 4, Ni after thorough heat treatment.
Curves 5 and 6, Mo after thorough and after only partial heat treatment.

Heating to a dull red heat failed to bring the molybdenum target to a final state; curves taken at this stage are different in form at low voltages from those taken after the target had been glowed out at a bright red heat (curves 5 and 6, Fig. 3). Also a maximum value of the ratio was reached at 315 volts in this stage instead of at the final value

of 356 volts (curves 1 and 2, Fig. 4). After the target was heated to a bright red heat a few times further heating produced no changes in the shape of the curves.

Breaks are found in the curves for both iron and molybdenum taken before the final state was reached. (No curves of this kind were taken for nickel.) These breaks, however, are not found at the same voltages

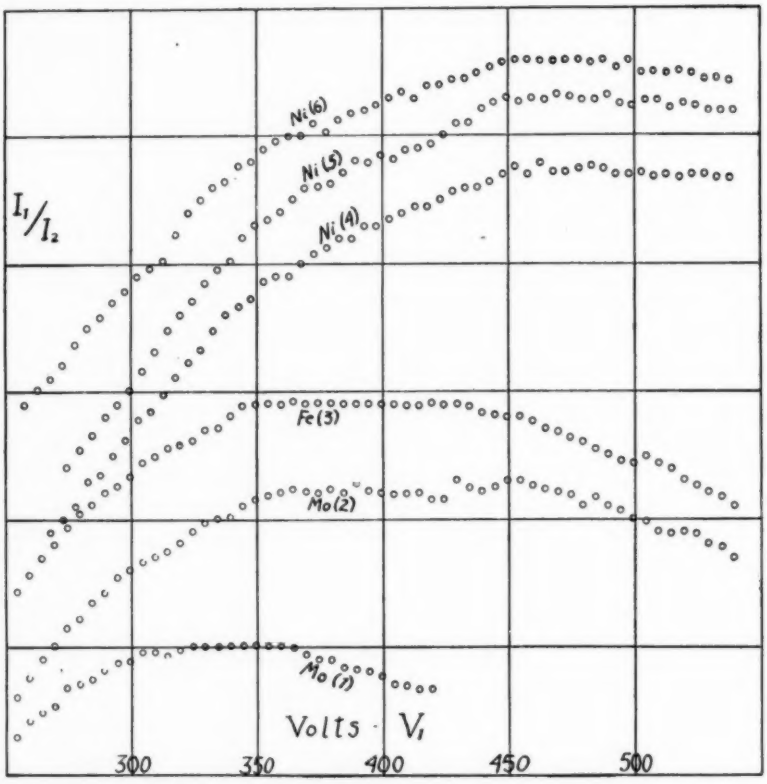


Fig. 4. Curves in region of maxima, 250-550 volts. Different scales of I_1/I_2 are used.
Curves 1 and 2, Mo after partial and thorough heat treatment.
Curve 3, Fe after thorough heat treatment.
Curves 4, 5 and 6, Ni after thorough heat treatment.

as are those for the heat-treated targets and are in general less definite, with more gradual curvature. Even after the final state was reached the ratio at any given voltage might vary a few percent from one set of runs to the next, but the position of breaks was not affected by the change of ratio.

Curves 1 and 2, Fig. 2, show the general variation of I_1/I_2 with velocity of impact up to 1500 volts, for iron before and after glowing

out the target. Curves 3, 4 and 5 show results for molybdenum untreated, after being heated to dull red heat, and in its final state; curve 6 is for nickel thoroughly heat-treated.

Fig. 3 shows the region 2 to 20 volts. Curves 1, 2 and 3 show results for iron taken at different times, all after heat treatment. In the region 7 to 10 volts the slope of the curve was sometimes positive and sometimes negative, but was always set off from the regions adjoining it by

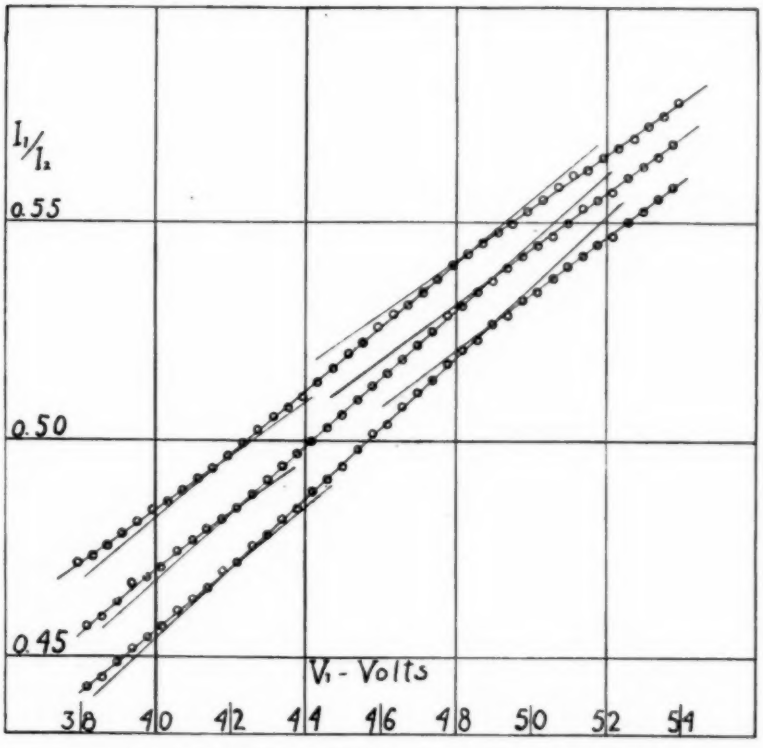


Fig. 5. Secondary emission curves for Fe, 36-56 volts.

changes of slope. Curve 4 is for nickel and curve 5 for molybdenum after careful heating. Curve 6 shows the results for molybdenum after heating to a dull red heat; there seems to be no connection with curve 5. In order to avoid confusion in plotting, these curves are not all plotted to the same scale of I_1/I_2.

Fig. 4 shows the region of the maximum, with I_1/I_2 plotted on different scales for different curves. Curve 1 is for molybdenum after partial treatment; the maximum value of I_1/I_2 is 1.205 secondary electrons per primary electron. The other curves are all for targets in

the final state and are as follows: curve 2, molybdenum, with maximum value of I_1/I_2 equal to 1.284; curve 3, iron, maximum value of 1.323; curves 4, 5 and 6, nickel, with maximum values of 1.282, 1.280 and 1.253 respectively.

TABLE I

Critical primary potentials for iron

Critical potential (volts)	Weight factor	Sign	General breaks	Soft x-ray levels (Thomas)	Critical potential (Stuhlman)
....				....	3.3
7.3	10	+	+7.3	7.3	8.5
11.6	10	−	−11.6	11.1	10.4
14.4	8	+	+14.4	14.1	
	4		+16.2	16.5	
18.3	4	+		19.4	
22.6	4	+		....	
25.0	2	−		24.3	24.3
29.0	1	+	+30.6	28.8	
....				34.3, 37.5	
43.6	2	+		41.2	
46.5	4	+		48.	
....				51.3	50
55.5	2	−		54.6	
63.8	3	−		62.	
....				67.6	
70.4	3	−	−70.6	....	
....				75.3, 82.7	80
85.1	1	+	85.1	87.1	
....				91.2	
97.6	4	−		94.8	
....				103.5, 112.2	
119.4	1	−		....	120
				125.7	
....					
157.2	2	−		seventeen	160
175.6	2	−		potentials	171
193.3	(?)	−		omitted	200
227.3	(?)	−			
257	2	−			
290.	1	−	290	288.6	
....				303.7, 331	
348	5	−	348	....	
390	1	−		....	
455	2	−		....	
....				639	
720	1	−		704.3	
....				818.5	
1040	?	+		....	
1370	?	+		....	

An indication of the agreement of the results for iron in the region 38 to 54 volts is given by Fig. 5. This region is more satisfactory than the average, however. In particular the region 100 to 400 volts is difficult to interpret; what appears to be gradual curvature in this region may be due to a number of small breaks. Above 500 volts in

iron changes of slope seem to occur at a few fairly definite points in good agreement on all curves; but corresponding points for nickel and molybdenum are hard to locate.

In Table I the first column gives the critical potential for secondary emission from iron determined in the present investigation. In accordance with the suggestions followed by Thomas,[13] the value of the work function for iron, 5 volts, has been added to the observed values. The

TABLE II

Critical primary potentials for nickel

Critical potential	Weight factor	Sign	General breaks	x-rays levels (Thomas)
6.2	2	+		.....
9.3	3	−		8.6
9.9	3	−	−9.9	.....
11.8	5	+		11.74
15.1	3	+	+15.1	14.6
....				16.56, 18.0
22.6	4	+		22.2
....			+23.5	.....
24.4	2	+		
....				27.25
31.4	5	+	31.4	30.97
35.0	2	+		34.6
....				39.8, 44.65
48.2	3	+	+47.	.....
....				51.3, 54.8
58.5	1	+		57.4
....				65.6
72.6	?	−	71.9	71.9
....				79.8
84.5	1	+		87.2
....				91.2, 94.9
....			98.3	.....
			106.5	.....
115.3	?	−	−115.	116.6
172	?			(fourteen omitted)
262	2		262	265.9
....				280, 286.5, 294.9
....				311.5, 341.3
356	5	−	365	....
455	5	−	455	.....
503	1	−		
....				774, 833.4
....				948, 1017.3

second column gives an estimate of the importance of the break based on intensity and on definiteness of location. All breaks except those of weight (1) were shown with fair agreement by all curves over the ranges concerned. The third column shows whether the break was due to an

[13] C. H. Thomas, Phys. Rev. **25**, 322 (1925).

increase of slope (+) or a decrease (−). The fourth column gives breaks which appear when curves with much larger voltage intervals are plotted, so as to average out all breaks which do not result in a change of slope which persists over at least a considerable voltage interval. The fifth column gives results by Thomas for soft x-ray levels for iron. Breaks observed by Thomas since the paper to which reference is made was published are included. Seventeeen breaks between 130 volts and 280 volts have been omitted in this column since comparison between the few values in the first column and the large number found here by Thomas would be without significance. The sixth column gives results for critical potentials in secondary emission from iron reported by Stuhlman.[12]

TABLE III

Critical primary potentials for molybdenum

Critical potential	Weight	Sign	General breaks
4.9	2	+	
7.3	1	−	
8.4	8	−	−8.5
12.7	5	+	+12.7
15.0	2	+	
16.5	1	+	
22.5	3	+	
30.5	4	+	
37.4	2	+	
41.9	3	−	−42
50.7	?	−	
53.9	1	−	
59.3	1	−	
65.8	0	+	
79.5	3	−	−79.
82.8	1	−	
101.9	?	−	
111.4	?	−	
131.3	0	−	
206.5	1	+	
298	2	−	−298
356	4	−	−356
473	1	−	

Table II similarly gives the results of the present investigation with nickel and the unpublished results obtained by Thomas for soft x-ray levels for nickel. Again 5 volts for the work function of nickel have been added to the results of both observers to give the data of columns 1 and 4. Table III shows the breaks observed in secondary emission from molybdenum; 4.3 volts have been added for the work function of molybdenum. No detailed data are available for comparison.

Discussion of Results

Tables I and II show good agreement between columns 1 and 5 up to 40 volts. Above that voltage column 5 begins to have more values than column 1 and above 100 volts a comparison would be of no value. The curvature observed in this region in the secondary emission curves may be due to a large number of breaks, each too faint to be located separately. If several breaks of column 5 are interpreted as a single break in column 1 the agreement should disappear. However, no breaks are found by Thomas between 331 and 639 volts for iron and between 341 and 774 volts for nickel, while one of the more definite points in the secondary emission curves, the point at which the ratio reaches a maximum, comes in these regions, at 348 volts for iron and at 455 volts for nickel. Therefore it appears that, in the two investigations different effects have been studied at high voltages and that in the present work the effect of photo-electric emission due to x-radiation is not detectable because of larger effects which mask it.

It has been shown by Farnsworth[11] that a negative break may be accounted for by assuming that inelastic impacts begin to occur at critical voltages so that, after such a collision, neither the primary electron nor the electron with which the collision occurs has sufficient energy to escape from the metal. It may be noted that if the work function of nickel and iron is 5 volts, all electrons with a velocity less than 5 volts will fail to escape from the metal so that the curves might be expected to show negative breaks at the critical potentials for inelastic impact, followed by weaker positive breaks at an interval of 5 volts.

The meaning of the decreasing value for the ratio with increasing velocity of impact at high velocities is in doubt; there is no apparent reason why the probability of escape after a collision should decrease with increasing velocity unless a large part of the primary electrons penetrate to a comparatively great depth before making a collision, so that secondary electrons are less likely to escape.

In conclusion the writer wishes to thank Professor K. T. Compton, at whose suggestion this problem was taken up, for his constant interest and frequent assistance in the work.

Palmer Physical Laboratory,
Princeton, New Jersey.
May 20, 1925.

NEGATIVE ION EMISSION FROM OXIDE COATED FILAMENTS

By Henry A. Barton

Abstract

Using a tube described by Smyth,[1] it was discovered that oxide-coated, platinum filaments emit negative ions as well as electrons. These ions were shown to be due not to gas in the tube or to gas absorbed by the filament, but to disintegration of the oxide coating itself. Electro-magnetic analysis of these ions, described in this paper, gave the value of m/e as about 33 with reference to hydrogen ions and indicated that they consisted only of negative, singly charged, molecular oxygen ions. No evidence of the emission of any positive ions was obtained. This negative ion emission apparently begins at a lower temperature than electronic emission, and increases with temperature, but less rapidly than the electronic. The contribution of the negative ions to the space charge is appreciable because of their relatively large mass, causing the space charge limited current for a given voltage to be less than for a similar non-coated platinum filament. Certain observations by other experimenters are discussed and shown to be in support of the above conclusions.

DURING a study of the ions formed by electron impact in argon,[2] the writer observed negative ions in large numbers. These were first thought to be formed by argon atoms but subsequently it was discovered that they were produced even when no argon was present in the experimental tube. A more careful examination of their behavior indicated that they came from the filament and were of smaller mass than argon atoms. The filament then in use was a strip of platinum coated with barium and strontium oxides. After substituting a thoriated tungsten filament the negative ions were no longer observed.

More recently a direct study of this phenomenon has been made. The experimental tube was the one described recently by Smyth[1] modified only by the removal of the gauze electrode next to the filament. The result was a simple arrangement for the accurate electromagnetic analysis of the particles from a hot source. A new platinum strip was mounted as a filament and a careful search made for negative ion emission. None was observed. The strip was then taken out and given an oxide coating by the following process: Two sticks of paraffin one containing $BaCO_3$ and the other $SrCO_3$ were touched to the strip

[1] Smyth, Phys. Rev. **25**, 452 (1925).
[2] Barton, Phys. Rev. **25**, 469 (1925).

alternately while it was maintained at a temperature just too low to give visible radiation. After each application time was allowed for the paraffin to burn off. When a good coating was obtained, the strip and leads were heated red hot in a flame to remove the last traces of hydrocarbons. They were then immediately installed and the tube evacuated. In the subsequent work the pressure in the tube was of the order of 10^{-4} mm.

With the filament at red heat, negative ions of the same mass as before were again observed in large numbers, thus proving that the source of these ions was the oxide coating. The range of m/e values from about 5 to 95 times the value for the hydrogen nucleus was ex-

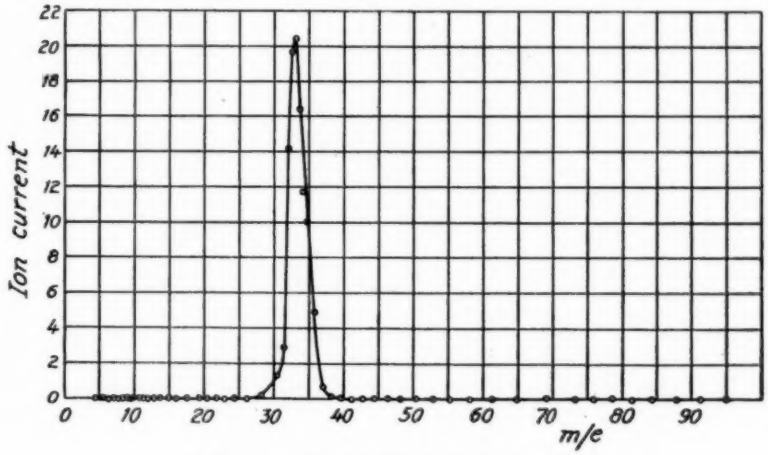


Fig. 1. Mass spectrum of negative ions.

amined and only one group of negative ions was detected. A typical mass spectrum is given in Fig. 1. The fields were then reversed and an attempt made to detect positive ion emission. The m/e ranges examined included those corresponding to barium and strontium atoms, each with single or double charge, and also the hydrogen range. No positive ions whatever were observed. This checks a previous result with the first coated filament.

Identity of the ions. The negative ions observed had an apparent m/e value of 33. The m/e scale had been calibrated by known positive ions and may have been slightly inaccurate for negative ions because of lack of perfect reversibility of the electromagnet used. However, C_2^-, $(CO)^-$ and A^- ions were certainly not present. The paraffin sticks were tested for chlorides and none found to be present. The conclusion, therefore, is that the ions are oxygen molecules, i.e. O_2^-.

Other results. The apparatus was not adapted to a careful study of thermionic emission and no further results were obtained except some determinations of the variation of ion current with the temperature. These merely indicated inconclusively that the ions were first emitted at a temperature too low for electron emission and increased in number as the temperature was raised well into the range in which the electron current was large.

The evidence does not clearly indicate whether the O_2 molecules came off the filament already charged or picked up an electron after emission. The fact mentioned in the previous paragraph favors the former process.

The objection may be raised that not enough time was allowed for the absorbed gases in the oxide coating to be evolved. This objection might be valid in the case of the second filament but not in the case of the first, which had stood continuously in a high vacuum (except for argon at low pressures) for several months and had been burned two or three hundred hours at least.

Discussion

The above conclusions receive indirect support from the earlier experiments of several observers. For example, Wehnelt and Jentsch[3] observed that at a given temperature the current from a Wehnelt cathode never quite reached a saturation value as the applied voltage was raised. This is different from the behavior of a pure metal filament in a high vacuum but analogous to its behavior in the presence of a small amount of gas. In other respects oxide filaments have similar properties to pure metal filaments so it is quite likely this difference is due to the oxygen gas which is produced. The nature of the action is not clear.

Fredenhagen[4] observed (1) that the oxide disappears much more rapidly if the filament is heated with a properly directed field applied than with no field, (2) gas is given off when the cathode is in action, and (3) the metal under surface shows corrosion as if an alloy had been formed with the residual barium and strontium metals. The first of these suggests strongly the formation of O_2^- ions. This is also supported by Horton's[5] conclusion that the conductivity of hot oxides is partly electrolytic. The third observation is in line with the recent suggestion

[3] Wehnelt and Jentsch, Verh. d. D. Phys. Gesell. **10**, 605 (1908).
[4] Fredenhagen, Phys. Zeits. **15**, 21 (1914).
[5] Horton, Phil. Mag. **11**, 505 (1906).

of Koller[6] that the emissive property of the Wehnelt type of filament is due to the deposit of a surface film of the metal reduced from the oxide.

The nearest approach to the writer's work has been done by Schmidt[7] and his collaborators. They found that no positive ions were given off by heated oxides of cadmium and zinc although many salts of these metals do yield positive ions. It appears to be characteristic of oxides that the metal atoms are not emitted, at least not as ions. In regard to the emission of negative particles by these oxides, Schmidt merely mentions their action as Wehnelt cathodes emitting electrons. The construction of his tube apparently did not permit distinguishing between electrons and negative ions.

The effect of the negative ions in contributing to the space charge is very simple. Where the current as limited by space charge consists of two parts, i due to electrons (mass m), and I due to negative ions (mass M), Langmuir's equation for cylindrical electrodes may be rewritten

$$i\sqrt{m}+I\sqrt{M}=(2\sqrt{2}/9)\sqrt{e}\,V^{3/2}/r\beta^2$$

where e is the electronic charge, V the applied voltage, r the radius of the receiving electrode and β a geometrical constant. Since I is small compared with i, the latter is practically the observed total current. Therefore the total current is given approximately by

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V^{3/2}}{r\beta^2}-I\sqrt{\frac{M}{m}}.$$

Although I is small, $\sqrt{M/m}$ is quite large so that to obtain the same space charge limited current from an oxide coated filament as from a plain filament, it is necessary to apply a higher voltage. Katsch[8] has recently compared filaments of several types in identical geometrical situations. As would be expected from the above consideration, he finds it necessary to apply a larger potential to get the same current in the case of oxide coated filaments than in the case of tungsten or thoriated tungsten filaments.

The writer wishes to thank Professor K. T. Compton and Dr. H. D. Smyth for their encouragement and helpful suggestions.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
June 2, 1925.

[6] Koller, Phys. Rev. **25**, 671 (1925).
[7] Schmidt, Ann. der Phys. **75**, 337 (1924); contains summary of earlier papers.
[8] Katsch, Zeits. f. Techn. Phys. **5**, 11, 505 (1924).

THE PERSISTENCE OF THE RADIATION EXCITED IN MERCURY VAPOR

By Lucy J. Hayner

Abstract

A photographic method was used. Light from an intermittent mercury arc passed through a quartz cell containing Hg vapor at 40° to 100°C, and then together with the excited radiation through a hole in a rotating sector into a spectrograph. The sector was mounted on the shaft of the commutator which operated the arc. Thus for λ2537 a trace was obtained on the plate, whose length depended on the time of persistence of the radiation, the time scale being determined by the speed of rotation. Measurements of the blackening showed that the decay was exponential. The time to decrease to intensity $1/e$ came out 4.0×10^{-5} and 6.8×10^{-5} sec. for cells of length 1.6 and 3.2 cm respectiyely. For the arc alone in a tube of 0.9 cm radius the constant was 0.6×10^{-5} sec , while for the arc at the center of a bulb of 3 cm radius the constant was 5.5×10^{-5} sec, The decay was found to be independent of the vapor pressure from .006 to .27 mm for the cell and from .05 to 1.7 mm for the bulb. No persistence was observed when the cell did not contain distilling mercury or when it was sealed off from the pump. Fresh mercury seems to be necessary and also the absence of impurity. It is interesting to note that the time constants are of the order of magnitude of the times required for atoms at the temperatures involved to go without impact from the center to the wall of the cell.

IN A RECENT series of experiments Webb[1] studied by an electrical method the life of the resonance radiation λ2537 in mercury vapor. The radiation was excited by electron impacts under voltage sufficient to lift the valence electron to the $2p_2$ orbit. His results gave pressure and dimension relations not in agreement with those required by the "imprisonment theory" of repeated absorption and re-emission. Accordingly a metastable state for $2p$ was postulated. In this case the life of the radiation in the apparatus must depend largely upon the motion of the excited atoms. Approximate calculations based on this assumption agreed well with the experimental facts. The present paper describes experiments made to determine the persistence of λ2537 excited by resonance absorption in a vessel containing mercury vapor, a case in which the process of absorption and re-emission must play an important part. The rate of decay of this radiation excited by striking an arc was also measured.

[1] H. W. Webb, Phys. Rev. **24**, 113 (1924).

METHOD

A photographic method was used. This had a great advantage over the electrical method in that the spectral lines could be studied separately. It had the disadvantage, however, that a large amount of radiation was necessary. The resonance line λ2537 could not be produced below the ionization potential with sufficient intensity and it was therefore necessary to use the radiation λ2537 from an arc for the excitation of the resonance radiation. Thus the complex arc spectrum was always present during the excitation.

The apparatus is shown schematically in Fig. 1. The source *A* was a hot cathode arc in a quartz flask. For the study of the fluorescent radiation excited in a separate vessel, an evacuated quartz cell *B*

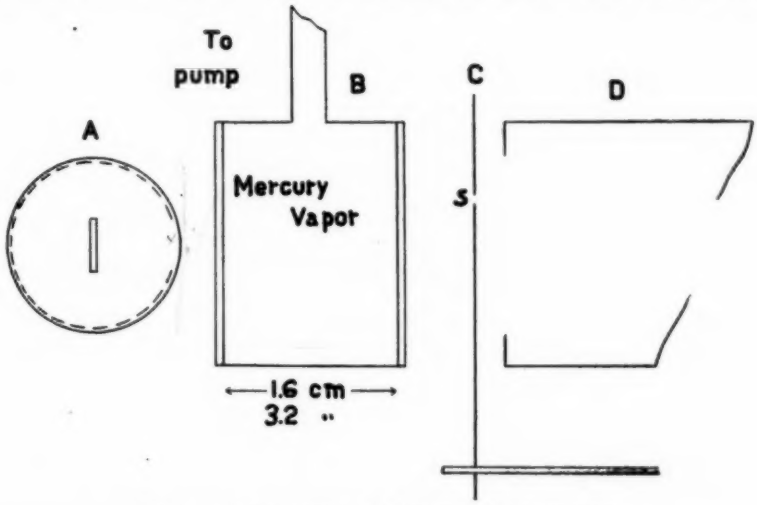


Fig. 1. Arrangement of photographic apparatus.

containing mercury vapor was placed between the source and the quartz spectrograph *D*. A disk *C* having near its circumference a small hole *S* which upon rotation of the disk passed the end of the collimator tube of the spectrograph, acted as a long slit, different parts of which corresponded to different instants of time. This disk was mounted on the axis of a commutator and could be adjusted with respect to the commutator so that the potential exciting the source could be removed at any desired point in the field of view of the spectrograph. The curved trace on the photographic plate beginning at this point revealed the subsequent history of the radiation. The speed of the disk and the law of blackening of the photographic plate were alone needed for quantitative measurement of the rate of decay of the radiation.

Apparatus

The mercury arc source was contained in a commercial quartz flask of 150 cc capacity, having a neck, 1.8 cm inside diameter and 9 cm long, sealed with DeKhotinsky cement to a hollow brass plug which was sealed in turn to a glass tube supporting the electrode wires and pumping tube. The flask was mounted in an upright position with a small amount of mercury in the bottom. An electric heater surrounded the bulb. The temperature of the flask was measured by means of a copper-constantan thermocouple attached to the outside of the bulb. The vacuum system consisted of a diffusion pump and forepumps. All observations were made at gas pressures below the limit of a McLeod gauge connected to the flask.

The source of electrons was an equipotential hot cathode of oxide coated platinum. The heating element was of 0.05 mm platinum, and insulated from it by mica was a sheath of 0.16 mm platinum making electrical contact with the heater at one end by a tongue. The sheath was coated with barium and strontium oxides. Heating currents of from 9.5 to 13 amp. were used. Such a cathode gave ample emission at bright red heat and lasted several months under almost daily use with arc currents as high as 2 amp. The anode was a cylinder of nickel gauze, 1.6 mm spacing, 1.8 cm in diameter and 6 cm long. For testing the behavior of the radiation excited in the cells it was necessary to have the arc in a tube of small diameter in order to insure that the radiation from the arc would decay very rapidly upon removal of the exciting potential. The electrodes were, therefore, suspended in the neck of the flask, the anode being in contact with the quartz wall. The radiation passed to the optical system through a slit in the anode.

Since each record on the photographic plate was composed of hundreds of superimposed photographs, it was essential that the commutator and disk be accurately constructed. An excellent commutator was built by the research mechanician, Mr. S. Cooey. The heavy commutator disk, 12.7 cm in diameter and 2.5 cm wide, was divided into 24 sections separated by 0.8 mm of mica, accurately spaced to about .0025 mm. Each section could be connected to either of two slip rings, thus providing for an exciting and a reverse potential. The contacts to the commutator and slip rings were made by hard carbon brushes. The brush on the commutator was ground to a knife edge and placed perpendicular to the surface so that the bearing edge was not more than 0.5 mm wide. The shaft was mounted in ball bearings

and the whole so nicely balanced that it was run for periods of three or four hours without appreciable chattering or heating, even at speeds as high as 70 r.p.s.

The disk *C* was of aluminum, 20 cm in diameter, and was mounted on a steel face plate at the end of the shaft. Corresponding to each pair of commutator sections was a hole (*S*, Fig. 1), 0.3 mm in diameter, the small size being necessary to obtain sufficient resolution in time.

Two cylindrical quartz cells (See Fig. 1) with plane polished ends were used for the study of the radiation excited by resonance. In diameter they were 2.5 cm, and in length 1.6 cm and 3.2 cm, respectively. These cells will be referred to as the short and long cells, respectively. Connection to the vacuum system was provided by a stem in the middle of each. For temperature control this stem was jacketed close to the cell.

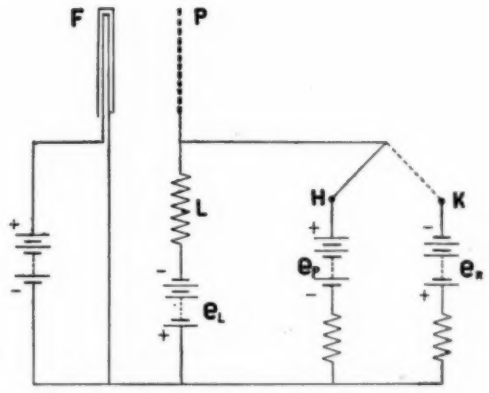


Fig. 2. Electrical circuit of the arc.

Experimental Procedure

The essentials of the electrical circuit of the arc are shown in Fig. 2. *P* is the anode and *F* the filament. Two adjacent segments of the commutator are represented by the points *H* and *K*. While *P* was in contact with *H*, usually about 7×10^{-4} sec., the arc was excited by a positive potential e_p. As the brush passed from the segment *H*, the positive potential was removed from *P*, and after an interval of time corresponding to the passage of the brush over the mica section, the reverse potential e_r was applied by the segment *K*. The commutator and disk were adjusted so that the positive voltage cut-off came after the hole in the disk had traced a line several millimeters long on the

photographic plate. The exact position of this cut-off was determined from a photograph made while rotating the disk slowly by hand. To test the uniformity of the different parts of the arc, etc., a check photograph with the disk rotating but with an uninterrupted positive voltage on P, was taken on each plate. This was necessary since patches of unusually intense radiation were occasionally observed in the arc, and there were blemishes in the windows of the quartz cells.

Precautions were taken to eliminate errors due to sparking as the brush left the "live" section of the commutator, and to leakage over the mica insulation. Most of the photographs were taken at arc currents of a few tenths of an ampere, so that with a non-inductive circuit, sparking was reduced until it was barely visible in a darkened room. Again, a leak L, with or without a reverse voltage e_L, was introduced to take care of the period during which the brush was on the mica insulation. Also, reverse voltages were maintained on the "dead" commutator sections. Out of at least 50 photographs of the arc alone, some with exposures of several hours, not one gave evidence of faults in commutation. Furthermore, the entire mica insulation corresponded to only 1 mm on the plate, whereas with the long cell in the system the persistent radiation caused a trace 15 mm in length. The effect of vibration of the commutator system with respect to the photographic plate was found to cause an error on the plate of only 0.2 mm, corresponding to an error of less than 3×10^{-6} sec.

Photographs of the arc with electrodes in the neck of the flask were first taken as described above. The quartz cell was then introduced between the arc and the disk and photographs taken as before, using each cell at various speeds of the disk, with temperatures ranging from 40°C to 100°C.

The photographic densities on the plate were measured by means of a small bismuth-silver thermocouple mounted as the cross-hair in a microscope of approximate magnification 2. This magnification, together with the small size of the thermocouple, 1/3 mm by 1/6 mm, gave sufficient resolution for measurements with even the most rapid rate of decay observed.

The photographic densities were translated into intensities by means of test plates developed either in the same bath or under similar conditions. The exposures on the test plates were obtained by photographing a mercury arc of constant intensity for varying intervals of time. The photographs to be measured, on the other hand, were made under the condition of a constant exposure time but varying

intensity. It is well known that for very short times of exposure or for very low intensities the reciprocity law no longer holds, but the work of Harrison and Hesthal[2] shows that for panchromatic films in the wave-length region under consideration the density-log time curves and the density-log intensity curves have the same slope over their linear portions. Only those plates were chosen for measurement, therefore, whose densities lay on the straight part of the density-log exposure curve. When the check photographs, taken with an uninterrupted positive voltage on the anode, showed variation in density over the length of a trace, a correction was applied to reduce to a uniform initial intensity.

Results

The intensity-time relation for λ2537 from the arc alone is shown by Curve (*a*), Fig. 3, starting from the instant of commutation. The intensity of the radiation falls off in a manner approximately exponential with the exponential constant 1.7×10^{5} sec.$^{-1}$ This gives the time constant 0.6×10^{-5} sec. Besides a strong absorption of λ2537, the effect of the introduction of the cells into the path of the radiation was to decrease the rate of decay of that line. The longer cell produced the greater change. Curve (*b*) shows the decay of the radiation for the short cell in the system and Curve (*c*) that for the long cell. These curves show an approximately exponential decay with the time constants 4.0×10^{-5} sec. and 6.8×10^{-5} sec. for the short and long cells respectively. These times are roughly proportional to the lengths of the cells. The above curves are each the average of determinations made from several plates, and are not in error by more than 10 to 15 percent.

The persistent radiation from the arc directly transmitted through the cell after the cutting off of the voltage was insufficient to account for the persistence found with the cells. Curve (*a*) Fig. 3 shows a measurable persistence of λ2537 from the arc, but the rate of decay of this radiation was so rapid that at the time when the radiation measured with the long cell in the path had fallen to $1/e$ of its initial value, the arc radiation, even if uncorrected for absorption, would have been present with only 1/7000 the intensity actually observed. If corrected for the cutting down of the radiation from the arc by the mercury cell, about 98 percent as measured by the relative exposures necessary to give equal plate densities with the arc alone and with the cell in the path, the primary radiation is seen to be entirely negligible

[2] Harrison and Hesthal, Jour. Opt. Soc. of Am., **8**, 471, (1924).

after the first 2×10^{-5} sec. As a further check a photograph of the arc was made with the length of exposure necessary to produce a measurable plate with the long cell in the path. The trace on this much over-exposed plate had entirely disappeared at a time at which radiation of considerable intensity still persisted with the long cell in the system. These facts show clearly that practically all the persistent radiation coming from the cell was due to some process of absorption and re-emission by the vapor in the cell. The shape of the decay curve for

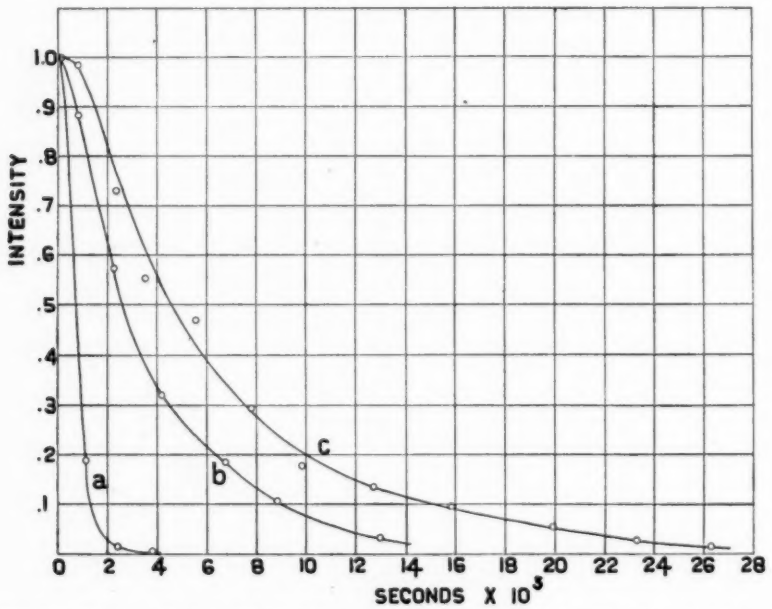


Fig. 3. Rate of decay of λ2537 from the source alone (a) and with the shorter cell (b) and the longer cell (c) in the system.

the first 2×10^{-5} sec. is distorted, however, by the persistent radiation from the arc. No correction can be made, since the method of correction depends upon the unknown processes involved in the persistence.

Over the range of cell temperatures investigated, 40° to 100°C, the rate of decay of λ2537 was found to be independent of the pressure as measured by the temperature at which the mercury condensed in the stem of the cell. The body of the cell was maintained at a higher temperature to prevent condensation on the faces. Thus the temperature of the liquid mercury in contact with the cell wall was always higher than that of the stem, so that the vapor pressure of the mercury in the cell was higher than that corresponding to the temperature

of the water jacket on the stem. That variation in the vapor pressure in the cell was brought about by the change in temperature of the water jacket is certain, since between the lowest and the highest temperatures employed there was a twenty-fold decrease in the transmission of λ2537.

It is of interest to note that upon introduction of the cell into the system the increased persistence of λ2537 was observed only when mercury from a drop in the cell was distilling into the stem connected with the vacuum pump. A photograph taken with the cell free from liquid mercury, but connected with the pump so that it contained mercury vapor at about 30°C, showed considerable absorption of λ2537 but no persistence greater than that accounted for by the arc alone. The explanation that at once suggests itself is that the persistence is present only near the surface of distilling mercury. Yao[3] found this condition necessary for the striking of a low voltage arc at 4.9 volts. Doubt is thrown upon this explanation by other photographs taken after the cell had been thoroughly baked, pumped and sealed off. In this case also there was no increased persistence, although mercury was distilling freely into the jacketed stem. It is possible that the condition for the slow decay is not the presence of freshly evaporated mercury vapor, but is the absence of traces of air or water vapor which might have been introduced during the sealing-off process. The cell, containing liquid mercury and connected with the pump, would constitute in itself an effective diffusion pump, so that only extremely pure mercury would be present in the body of the cell. It is well known that a small amount of air is effective in quenching the radiation λ2537 excited by resonance.

Discussion

Lack of data relating to the exceedingly complex processes involved in the persistence of radiation in a vapor makes an exact description of these processes impossible at present. The nature of the process of absorption of radiation by an atom and the effect of molecular impact during or after absorption are not understood. The character and the amount of dissipative absorption are not known. In the experiment described above all the lines of the arc spectrum were present during the period of excitation. Since these lines are absorbed by excited vapor it is probable that they play some part in the persistence.

There is reason to expect the presence in the cells of metastable atoms in the $2p_1$ and $2p_3$ states, resulting either from impacts of normal

[3] Y. T. Yao, Phys. Rev. **21**, 1 (1923).

mercury atoms with excited atoms in the state $2p_2$ or from the absorption of the strong arc line $2p_2-1s$ which lifts the electron to the $1s$ orbit from which two of the three possible transitions leave the atom in the metastable states $2p_1$ and $2p_3$.[4] The effect of impacts with the metastable atoms would be, in part, reversion to the $2p_2$ state and subsequent emission of λ2537. There is also the possibility of a mercury molecule formed by impact of a normal atom with an atom in the $2p_2$ state, although neither the ultra-violet nor green bands characteristic of the fluorescence of mercury at high pressures, and attributed to Hg_2, appeared on the plates or to the eye.

It is not clear, however, how the persistence of λ2537 may be related to the presence of such metastable atoms in the vapor. One possibly significant fact is, however, to be noted with regard to the above results. The times involved in the rate of decay of λ2537 were of the order of magnitude of the times required for atoms, having the mean velocity corresponding to the temperature used, to traverse the cell without impact. At 75°C the mean velocity of mercury atoms is 1.9×10^4cm/sec. In the case of the cell of length 1.6 cm, an atom would, on the average, traverse a distance equal to the length of the cell in 8.4×10^{-5} sec. For this cell the time constant was 4.0×10^{-5} sec. If, instead of the total length of the cell, the mean length (one-half) is taken, this mean time is 4.2×10^{-5} sec., which is very nearly equal to this time constant. In the case of the long cell the agreement is not so close but the times are still of the same order of magnitude. The experimental curves correspond closely with those calculated on the assumption of a uniform initial distribution of excited atoms throughout the cells and of the passage without impact of these atoms to the walls of the cell, where the energy of excitation is freed as radiation. However, with the vapor pressures used the probability of such a passage without impact is so small that such an explanation of the results by diffusion of excited atoms seems impossible, unless some new factor be assumed such as the compensation of the slower passage of the excited atoms, due to impacts, by the dissipation of the persistent radiation at impact.

Since the whole persistent process depends initially upon the absorption of λ2537, one would expect at least a part of the persistent radiation to result from repeated absorption and re-emission. Wood has shown that there is such diffusion of radiation in mercury vapor at .001 mm pressure.[5] If this is the only process effective, however,

[4] R. W. Wood, Proc. Roy. Soc. **A106**, 679 (1924).
[5] R. W. Wood, Phil. Mag. **23**, 689 (1912).

the absence of any dependence of the rate of decay on vapor pressure is difficult to account for, unless we may assume some compensating process such as dissipation at impact or a change in the wave-length of radiation emitted during impact. Even at a pressure as low as .001 mm the probability of a quantum of radiation diffusing through the cell without being associated with an atom at impact is small. There is evidence[6] for the dissipative effect of impacts in the decreased intensity of λ2537 excited by resonance absorption in pure mercury vapor at high pressures. At very high vapor pressures the time between impacts may determine the order of magnitude of the persistence, while between the low and high extremes of pressure there is possibly a pressure range over which only a small variation in rate of decay might be observed.

Persistent Radiation from a Mercury Arc

A study of the rate of decay of λ2537 from an arc struck at the center of a mass of mercury vapor, approximately a sphere 6 cm in diameter, was also made. The same quartz flask was used, but the hot cathode and anode were supported at the center of the bulb and a third electrode, a nickel mesh, lined the spherical quartz wall. By a method similar to that employed with the cells, photographs were taken at temperatures from 70°C to 150°C with several voltages on the outer electrode and several different reverse voltages on the anode after commutation.

The curves in Fig. 4 show the rate of decay of λ2537 from this arc. The persistence was very much longer than that observed with the arc in the neck of the flask. The curves are, like those for the cells, approximate exponentials, the time constant in this case being 5.5×10^{-5} sec. The difference between the geometry of the spherical bulb and that of the cylindrical cells makes any comparison involving dimensions very difficult. It is to be noted that the difference of potential between the electrodes after commutation made not the slightest difference in the rate of decay. The same curves were obtained for an open circuit as for reverse potentials from 1 volt to 50 volts. There seems, therefore, little doubt that the persistent radiation λ2537 in the mercury arc was due to the same cause as that in the cells, and is not to be explained by space charge conditions or recombination.

[6] Wood and Kimura, Phil. Mag. **32**, 329 (1916).

It is also to be noted that within the limits of experimental error the rate of decay of λ2537 from the arc in the bulb of the flask was independent of the vapor pressure over a range of pressures from .05 mm to 1.7 mm. The curve in Fig. 4 is drawn through points taken from photographs at 78°C, 100°C, and 140°C, as measured by a thermocouple attached to the outside of the bulb near the liquid mercury. Since the seal at the top of the neck of the flask was water cooled, there was considerable condensation at that point, so that the pressure of the mercury vapor was less than that corresponding to the temperature measured. The condensation, however, took place several inches from

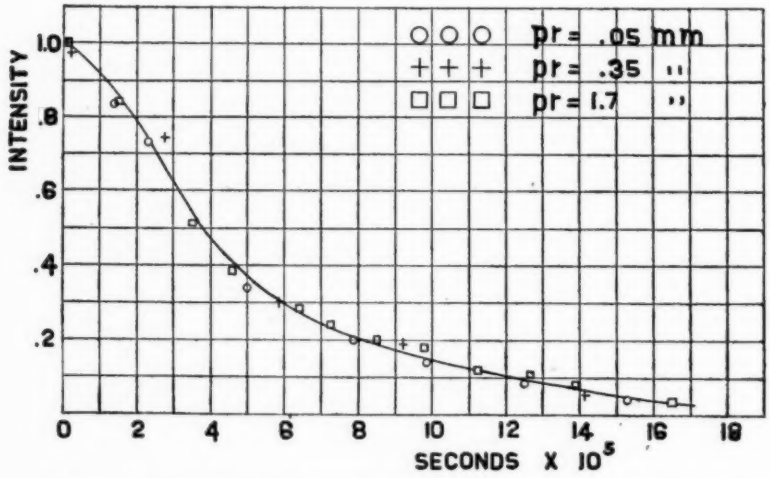


Fig. 4. Rate of decay of λ2537 from the arc in the bulb of the flask.

the top of the bulb, while the electrodes were immediately above the mercury surface. Furthermore, the increase in the intensity of the radiation and the change in the appearance of the arc make it certain that there was a large change in the vapor pressure. The rate of decay was so nearly independent of the vapor pressure that one curve was drawn through the circles, crosses and squares which give the experimental results for vapor pressures, computed as above, of .05 mm, .35 mm, and 1.7 mm, respectively.

At higher temperatures and greater currents the arc emitted after commutation a peculiar many-lined persistent spectrum, which was studied in detail together with the current conditions in the tube after commutation. The results of this study will be discussed in a later paper.

In conclusion I wish to express my indebtedness to Professor H. W. Webb, at whose suggestion and under whose guidance this work was done.

PHOENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
May 18, 1925

DURATION OF FLUORESCENCE OF MERCURY VAPOR

By R. N. Ghosh

Abstract

Discussion of experiments by Phillips, Wood and Vanderlingen.—It is suggested that the fluorescence observed with fresh vapor is due to absorption of light by diatomic molecules which thus acquire energy of about 7 volts. The persistence of the fluorescence is accounted for by assuming that many of these activated molecules transmit the energy to others by collisions of the second type, energy which is eventually radiated in several jumps corresponding to the bands observed. If such activated molecules are present, they should ionize Cs and K molecules mixed with them.

1. In a recent paper[1] M. N. Saha and N. K. Sur have pointed out that the chemical and physical activity of nitrogen in the experiments of Lord Rayleigh, can be explained by Klein and Rosseland's theory of collisions of the second type in which a transfer of energy takes place without radiation. According to Saha and Sur the molecules thus acquire energy[2] of 8.2 volts approximately, and the positive bands of nitrogen are due to the quantum emission of this energy by the activated molecules. The persistence of the glow beyond the electrode is due to the fact that all the moving molecules do not lose energy by free radiation but some communicate their energy to non-excited molecules; thus energy is carried beyond the electrodes. It seems to the writer that what we call fluorescence is nothing but an afterglow. In particular, the above explanation can be easily extended to the case of mercury vapor fluorescence as will be shown in this note.

2. Wood,[3] Phillips[4] and others have made an extensive study of the fluorescence of mercury vapor. Phillips observed that if freshly formed vapor of mercury obtained by briskly boiling the liquid be exposed to ultraviolet light, a green fluorescence distills over to the other cooler limb of the inverted U tube. The course could be traced for a length of about eighteen inches (47 cm). The fluorescence spectrum has been recently studied by Wood and J. S. Vanderlingen.[5] Their experiments indicated that only freshly formed vapor shows fluorescence.

[1] Saha and Sur, Phil. Mag. (Sept. 1924).
[2] According to others it is about 11 volts.
[3] R. W. Wood, Phil. Mag. **18**, p. 247.
[4] Phillips, Proc. Roy. Soc. **89**, p. 41.
[5] Wood and Vanderlingen, Astrophys. J. (Oct. 1921) p. 152.

The absorption spectrum of Hg vapor at high vapor density consists of (1) an asymmetrical band with a head at λ1849 which gradually creeps towards longer wave-lengths; (2) four lines, 2346, 2339, 2334, and 2331, which fuse together with rise of temperature forming a band which gradually pushes towards the shorter wave-lengths, and (3) a strong absorption band with head in close proximity to the line 2539.

With zinc spark excitation the fluorescence spectrum consists of (1) a structureless symmetrical band extending from the red down to the wave-length 3700, with its maximum at about 4850; (2) a symmetrical band with a maximum at about 3300, and (3) two small fluorescence bands with maxima at about 2539 and 2346 respectively. Restricting the exciting light to a definite wave-length by means of a monochromator, the aluminum line 1854 gave a fluorescence spectrum consisting of the green violet band (maximum at 4850). The authors[5] then tried zinc lines 2024, 2061, 2909 and 2138 by turns as the exciting light, and the fluorescent spectrum was found in each case to consist of the same green violet band, the ultraviolet band, and a faint band at about 2349. The authors conclude from these and other results that the absorption band 1849 is a complex one, so that excitation by various lines in that region is capable of producing fluorescence.

Neither the absorption nor the fluorescence due to lines below 1849 has been studied, but it can be concluded that when the exciting light is in the neighborhood of 1849, the fluorescing bodies must have absorbed the energy corresponding to that light and fluorescence with the emission of that energy. The energy corresponding to 1849 is about 6.7 volts. From the nature of the absorption bands and the fact that fluorescence does not occur in a cooling vapor but only with a freshly formed vapor,[2] it is concluded that the fluorescing molecules must be of the simplest type, that is diatomic. The exciting light from aluminum or zinc has no relation to the series spectrum of the atomic vapor. Hence, the formation of diatomic molecules cannot be attributed to an excited state of the atoms. The unstable diatomic molecules are given off[6] by the liquid when the temperature is either rising or constant. These molecules by the absorption of energy are brought into an activated condition; that is the energy of each molecule increases by about 6.7 volts. This energy is radiated out in jumps corresponding to 4850, 3300, and 2346. Wood[3] has shown that the fluorescent vapor is transparent in the ultraviolet region,

[6] A discussion will be found in "Origin of Spectra" by Foote and Mohler, p. 106, and Sommerfeld, English edition, p. 440.

a fact which lends support to the above view about the activated state of the molecules.

It is now an established fact that band spectra are due to molecules. There are three types of energy associated with energy of radiation by a molecule, (1) the electronic energy, (2) the energy of atomic vibration, and (3) that of the rotation of the molecule as a whole. Corresponding to the three types of activation we have three types of spectra. When energy of type (1) is quantized we obtain broad bands, say 100-300A wide; type (2) when quantized gives rise to bands 5-10A wide, while type (3) gives rise to the fine structure of the bands corresponding to type (2). Now in the case of the fluorescence spectra of mercury vapor we have seen that continuous bands with maxima are obtained. The continuity of the band on the longer wave-length side beyond the maximum is a departure from the general rule. This is probably due to the frequency of the mutual collisions between two molecules, resulting in intramolecular change of the electrons.[7] The maxima 2346, 2539, 3300 and 4850 may be considered to be the steps by which the quantized energy is radiated.

The prolongation of the path of the fluorescent vapor in Phillip's experiments can be explained on the present view of the activated state of the molecules. Ordinarily, when mutual collisions between atoms in the activated state and those not excited, are not very probable, the energy is freely radiated out by the excited ones after 10^{-8} sec. Wood[8] has recently measured the time interval between the excitation and the appearance of fluorescence of Hg vapor, and found it to be of the order of 6×10^{-5} sec. Total duration of fluorescence is of the order 3×10^{4} sec. The duration of the excited state of the molecules of Hg vapor will be of the same order; hence, if there was no collision between an activated molecule and a non-activated molecule, the duration of fluorescence or the path of the moving vapor in the fluorescent state cannot be very long. But the high vapor density increases the possibility of collisions of the second type to a great extent, and hence the whole column in Phillips' experiment is filled up with glow, due to the free radiation by a part of the activated molecules, the remainder transferring their energy to non-excited molecules, thus carrying the energy far from the excited region.

Wood's[9] observation that the intensity of fluorescence of iodine molecules is diminished by the addition of fresh iodine molecules, can be

[7] See Lenz, Phys. Zeits. **21**, p. 691 (1920).
[8] R. W. Wood, Proc. Roy. Soc. vol. **99**.
[9] R. W. Wood, Researches in Physical Optics, p. 80.

easily explained on the above view. What happens is that when fresh molecules are added the probability of collision increases, and therefore the activated molecules transfer their energy to non-excited molecules. Hence, the amount of free radiation at any instant diminishes.

We have seen that the fluorescent mercury vapor is loaded with energy of 6.7 volts; hence, when these molecules are mixed up with caesium or potassium vapor they should be ionized, since the ionization potentials of these are below 6.7 volts.

The author gratefully acknowledges his deep thanks to Prof. M. N. Saha for his interest and help.

PHYSICS DEPARTMENT,
ALLAHABAD UNIVERSITY, INDIA.
January 29, 1925.

Note added in proof. Since the above was sent for publication Lord Rayleigh's experiments (Proc. Roy. Soc. **108**, 262, 1925) throw more light upon the phenomenon. The absence of λ 1850 ($1S$-$1P$) in the distilled vapor, though strong in the arc, supports the view expressed above. The exercised diatomic (unstable) molecule under the conditions of the experiment, dissociates into one activated (4.7 volts) and one non-activated atom, the former radiating λ 2537 ($1p_2$-$1S$). This view is supported by the fact that the electric field does not quench the line, since it originates from neutral molecules. It seems, therefore, that the energy of dissociation of the diatomic molecules is less than 2 volts. The presence of some lines in the distilled vapor is due to the activation of the atoms by collision with the energized molecules. No lines appear whose energy level is greater than 7 volts.

THE OPTICAL CONSTANTS OF MAGNESIUM AND ZINC CRYSTALS

By M. E. Graber

Abstract

Magnesium and zinc were prepared in the form of hexagonal crystals. Their optical constants (4500A to 6500A) were then determined by the crystelliptometer, polarimetric method. Plane polarized light at an azimuth of 45° was reflected from one of the six faces of the crystal which was placed successively in two principal positions in which the principal axis of the crystal was (1) perpendicular or (2) parallel to the plane of incidence. Two sets of optical constants (index of refraction, absorption index and reflecting power) were thus obtained for each metal. Both indices of refraction for magnesium were found to be less than .5 for wave-lengths within the visible spectrum. The indices of refraction for zinc were found to be greater than unity except for the shortest wave-lengths employed. The reflecting powers of both metals agree well with the comparison determinations available. No marked selectivity was found in the optical properties of either metal.

Introduction

THE most consistent values of the optical constants of metals have been obtained from analysis of the elliptically polarized light reflected from their surfaces. If the resultant elliptic vibration is resolved into components parallel and perpendicular to the plane of incidence, it is possible to compute the optical constants of the reflecting metal in terms of the amplitude ratio and the relative phase difference of these two components by means of Drude's formulas.

The first application of this method to absorbing crystals was made by Drude[1] and by Mueller[2] on lead and antimony sulfides which occur in nature as crystals.

Professor L. P. Sieg suggested that crystal elements be prepared to eliminate as far as possible errors due to different degrees of polish and heterogeneity of surface. Working under his direction, L. D. Weld,[3] C. H. Skinner,[4] G. D. Van Dyke,[5] and R. F. Miller[6] have

[1] P. Drude, Wied. Ann. **34,** 489 (1888).
[2] H. Mueller, Dissert. Gottingen (1903).
[3] L. D. Weld, J. Opt. Soc. Am. **6,** 67 (1922).
[4] C. H. Skinner, Phys. Rev. **9,** 148 (1917).
[5] G. H. Van Dyke, J. Opt. Soc. Am. **6,** 919 (1922).
[6] R. F. Miller, Thesis, University of Iowa, (1923).

studied the optical properties of selenium and tellurium, and obtained reasonably consistent results for all the optical constants involved.

The object of the present study was to determine the two sets of optical constants of magnesium and zinc crystals within the wavelength limits 4550A to 6500A.

Experimental Methods

The magnesium crystals were supplied by S. L. Hoyt of the General Electric Company, and W. A. Scheuck of the Western Electric Company. The zinc crystals were produced by three methods, (1) by breaking cylindrical zinc castings, (2) by melting zinc in an electric furnace

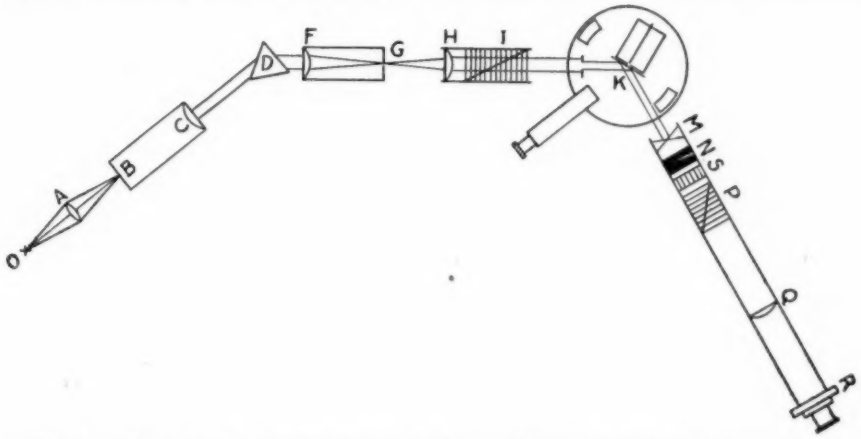


Fig. 1. Diagram showing arrangement of monochromator and crystelliptometer.

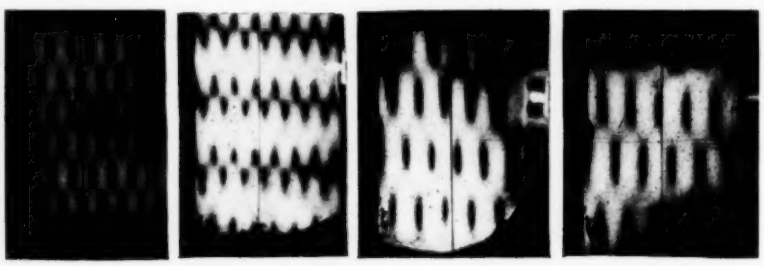
and attempting to draw it out as single crystals by means of a glass rod, (3) by permitting molten zinc to cool in a quartz tube and breaking the cast. In no case was a single crystal produced, but fracture yielded occasional lateral faces of a crystal.

The apparatus employed for light production and analysis consisted of an 11-ampere tungsten ribbon lamp *O*, a condensing lens *A*, a Hilger monochromator (type D32) *BCD*, a collimator *FG*, a crystal mount *K* and the crystelliptometer $M-R$, arranged as in Fig. 1.

After leaving the slit *G*, the beam of light passes through a focusing lens *H* and a pair of quartz wedges *I*, fixed with reference to each other. The optical axis of the wedge nearest the observer is vertical, while that of the second wedge is horizontal. Since the light vector perpendicular to the optic axis is faster than the other component, the vertical component of the incident light is slower for points to the left of the center line of the compensator while the horizontal component

is faster for all points to the right of the center line. The phase difference Δ at a distance x from the center is $cx+\nabla$ where c is the compensator constant and ∇ the original phase difference. The result is plane polarized light where $cx+\nabla=$ zero, π, 2π, etc. Great care was taken in the selection of crystals to insure a definite structure and one plane lateral surface. The crystal was mounted so that the plane of its face remained unchanged upon rotation through 90° about an axis perpendicular to that plane.

When the beam of plane polarized light at 0° incidence was reflected from the metallic surface the only effect was a rotation of the plane of polarization through 90° and we then had plane polarized light with an azimuth of 135° relative to the X-axis. Any change made in the angle of incidence produced a change of phase so that the reflected light became elliptically polarized.



A B C D

Fig. 2. Typical spot patterns

A. Direct transmission comparison plate, 4550A.
B. Tellurium pattern, 4960A.
C. Magnesium pattern, 6200A, horizontal position.
D. Zinc pattern, 6300A, horizontal position.

The crystelliptometer constructed by Dr. L. D. Weld consists of (1) a reticule M with vertical cross hair, (2) a rotator S consisting of a right and a left hand wedge the optical axis of each being in line with the direction of transmission, (3) a Glan-Thomson nicol P, (4) a converging lens Q, and (5) a photographic plate holder R. In passing through the rotator the periodically recurring bands of plane polarized light are rotated through an angle measured by ky where k is the rotation constant and y the displacement. The nicol interposed at P, Fig. 1, extinguished the vertical component of the beam. Wherever a plane polarized beam vibrating vertically exists, light cannot pass and dark spots result. When the light is elliptically polarized or has a horizontal component it will pass through the nicol and produce

an effect upon a photographic plate. The result on the plate is a spotted pattern the design of which depends upon the character of the eliptically polarized light. By comparing the spot-patterns for direct transmittion with the corresponding patterns for light reflected from the crystal surface it is seen that each spot is shifted vertically and horizontally. See Figs. 2-5.

Fig. 2A represents the photographic image produced by plane polarized light passing directly through the wedge systems of the rotator and the analyzer. The intersections of the vertical bands of plane polarization and the horizontal bands of 90° azimuth, are the spots of zero light intensity distributed in an approximately symmetrical order relative to the vertical cross hair.

In Fig. 2B the elliptic polarization of the light reflected from the plane face of a tellurium crystal has produced a displacement of all the spots of zero intensity in the same direction along the horizontal bands of equal azimuth and corresponding row displacements along the vertical bands of equal phase difference, but alternately in opposite directions. The bunching of rows is more clearly indicated in Fig. 2B than in the case of either magnesium, Fig. 2C, or zinc, Fig. 2D.

In measuring the photographic plates to determine the vertical spacing of the rows and the horizontal shift of the columns of spots from the position of phase difference $\Delta = \Pi$, a Gaertner 50 cm comparator was employed. Having marked the plate before photographing by placing it in a holder with small apertures and exposing to a light flash, it was placed upon the stage of the measuring microscope with the film side up.

Having adjusted the comparator so that the cross hair bisected the first row of spots, the micrometer screw was turned and readings taken for each row from the top to the bottom of the plate. The average of the shorter spacings was then found and designated q.

The same method was employed in measuring d the horizontal distance between successive spots and a, the horizontal shift of the columns of spots to the right of H.

HORIZONTAL SPOT PATTERN

			H			
1	2	3	0	4	5	6
0	0	0	0	0	0	0
0	0	0	0	0	0	
7	8	9	10	11	12	

Let $x_0, x_1, x_2, \ldots x_n$ be the absolute distances of the spots 0, 1, 2, ... n from H.

Then $x_0 = a$; $x_3 = d - a$;

$$x_1 + x_2 + x_3 = 3d + 3(d - a) = 6d - 3a \; ; \tag{1}$$

$$x_4 + x_5 + x_6 = 6d + 3a \; ; \tag{2}$$

$$x_7 + x_8 + x_9 = 3d + 3(\tfrac{1}{2}d - a) = 4\tfrac{1}{2}d - 3a \; ; \tag{3}$$

$$x_{10} + x_{11} + x_{12} = 3d + 3(\tfrac{1}{2}d + a) = 4\tfrac{1}{2}d + 3a \; ; \tag{4}$$

Adding (1), (2), (3) and (4)

$$x_1 + x_2 + \ldots x_{12} = \Sigma x = 21d \; ; \; d = \Sigma x / 21 \; . \tag{5}$$

Subtracting (1)+(3) from (2)+(4)

$$12a = (x_4 + x_5 + x_6 + x_{10} + x_{11} + x_{12}) - (x_1 + x_2 + x_3 + x_7 + x_8 + x_9) \; . \tag{6}$$

A comparison photographic plate was taken with the crystelliptometer in direct alignment with the collimator (Fig. 2A). Measurements of this plate determined the position of H, the value of d, and the vertical column spacing p.

The largest errors in the measurements of a and q are due to the difficulty in finding the true centers of area of the spots. Various methods of reducing these errors have been suggested but the variation in size and in spot intensity renders any one method inadequate. The value of d is more accurate when taken from the measurements on the comparison plate, since the spots are of more uniform size and the pattern more distinctly clear cut than in the plates taken with reflected polarized light. Large differences in the value of d indicated inaccurate measurements.

Drude's Formulas

If Δ represents the difference in phase and Ψ the change in azimuth of the two components of reflected light,

$$\pi - \Delta = (a/d)\ 360^\circ \tag{7}$$

where a is the shift of each column of spots from the position for $\Delta = \pi$ and d is the distance between columns.

Again $$\Psi = (q/p)\ 90^\circ \tag{8}$$

where q is the distance between adjacent rows of spots after reflection from the crystal surface and p is the corresponding distance before reflection.

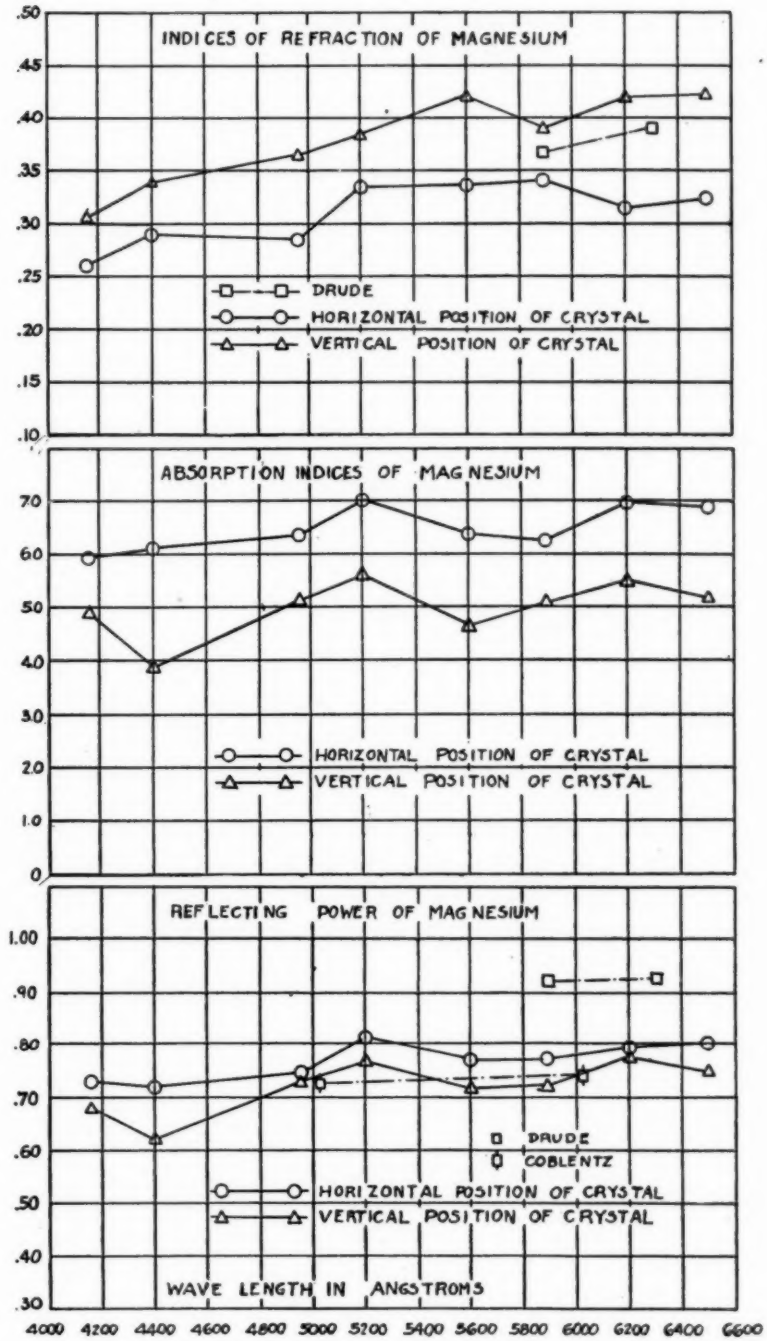


Fig. 3. Optical constants of magnesium.

In determining the optical constants of the crystal with its principal axis perpendicular and parallel respectively to the plane of incidence, the formulas used by Drude[7] and by Mueller were applied.

Results

With the angles of incidence ranging from 60° to 80°, the two sets of averaged optical constants obtained for magnesium are given in Table I.

TABLE I

Optical constants for magnesium

Wave-length	N_1	N_2	K_1	K_2	R_1	R_2
4160A	.260	.305	5.95	4.94	.730	.680
4400	.290	.340	6.10	3.87	.720	.620
4960	.285	.365	6.37	5.06	.745	.715
5200	.335	.385	6.97	5.57	.810	.765
5600	.337	.420	6.38	4.62	.785	.715
5890	.340	.390	6.25	5.05	.785	.722
6200	.315	.420	6.97	5.48	.795	.775
6500	.323	.423	6.94	5.18	.800	.745

The above results are plotted in Fig. 3.

The only values of optical constants for magnesium available for comparison purposes are those of Drude and of Coblentz. The indices of refraction for the vertical position of the magnesium crystal are in close agreement with Drude's results for polished magnesium surfaces. There is, however, a marked departure from Drude's results for absorption indices and reflecting powers. He obtained 11.8 as the absorption index of magnesium for wave-length 5890A, which results in the abnormally large reflecting power of 93 percent. Coblentz by direct measurements determined the reflecting power of magnesium to be approximately 72 percent for the same wave-length, which is within a few percent of the tabular values above. Toole's[8] observations indicate that Drude's high absorption was due to the surface mat developed by polishing. The magnesium crystals employed in this investigation lost their reflecting power in the course of a few weeks, and new crystals were substituted. Drude, Tate, and Toole agree that polishing increases the reflection and absorption coefficients of metals although the forms of the curves for the optical constants are not materially changed by polishing or by impurities. Tyndall[9] also found that although there was

[7] Drude, Ann. der Physik **32,** 584 (1887).

[8] Toole, Phys. Rev. **31,** 1 (1910).

[9] E. P. T. Tyndall, Phys. Rev. **21,** 162-181 (Feb. 1923).

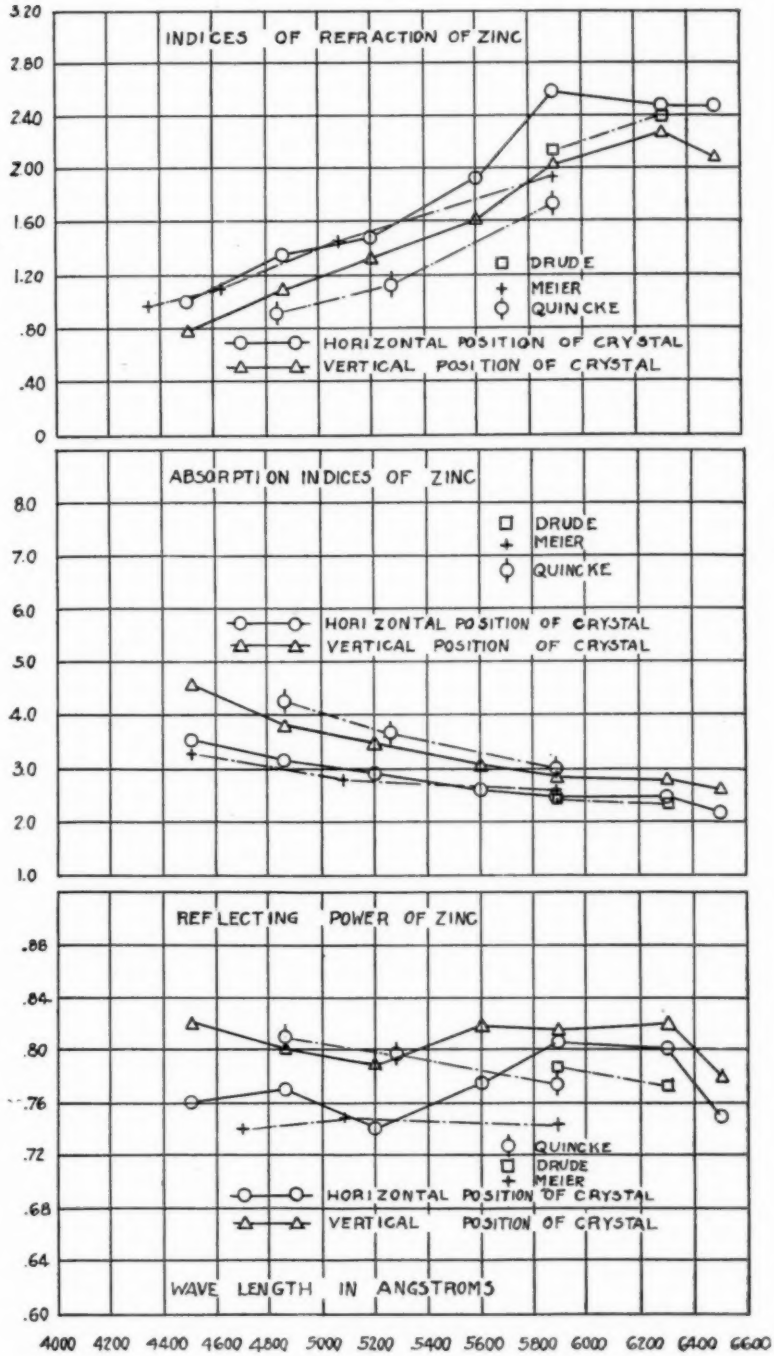


Fig. 4. Optical constants of zinc.

no agreement between his values of K in the case of molybdenite and those of Crandall, the general trend of their curves was the same.

The corresponding optical data for zinc are exhibited in Table II.

TABLE II

Optical constants for zinc

Wave-length	N_1	N_2	K_1	K_2	R_1	R_2
4550A	1.00	.78	3.55	4.58	.760	.820
4860	1.35	1.09	3.14	3.80	.770	.800
5200	1.47	1.32	2.94	3.49	.740	.790
5600	1.92	1.61	2.60	3.08	.775	.820
5890	2.58	2.02	2.29	2.86	.805	.815
6300	2.47	2.27	2.47	2.79	.800	.820
6500	2.47	2.07	2.15	2.60	.750	.780

The above results are plotted in Fig. 4.

The optical constants of zinc have been determined for 5893A and 6300A by Drude, for the range from 4310A to 6500A by Quincke, and for the range from 4413A to 6680A by Meier. Comparison of the results in Table II with those of the above authorities indicate that the writer's indices of refraction for the vertical position of the crystal lie between those of Quincke[10] and of Meier[10] for the range from 4550A to 5890A and below those of Drude[10] between 5890A and 6300A. The corresponding indices of refraction for the horizontal position of the crystal are larger than those of any other authority cited. The absorption indices for the horizontal position of the crystal compare well with those obtained by Meier[10] and by Drude while the corresponding indices for the vertical position of the crystal are reasonably close to those of Quincke.

The reflecting powers for both the horizontal and vertical positions of the zinc crystal are greater than any other available results beyond 5700A. The reflecting power for the horizontal position varies from 74 percent to 80 percent and for the vertical position from 78 percent to 82 percent. The higher reflecting powers obtained for the zinc in the crystal form are probably due to the fact that the crystal possesses nearly filmless and homogeneous surfaces along each of the principal directions, with distinctive optical properties depending upon the relative position of the axis and the angle of incidence. The drop in reflecting power at 6500A may be the beginning of a deep minimum observed by Coblentz[11] at 10,000A.

[10] Landolt-Bornstein-Roth Tabellen.

[11] Coblentz, Bur. Stds. Sci. Papers, No. 379, **16**, 251 (1920).

In conclusion the writer wishes to express his appreciation to the Physics Department of the University of Iowa for assistance rendered, especially to Prof. L. P. Sieg under whose direction the work was carried on, and also to acknowledge indebtedness to Dr. E. O. Hulburt for the use of his lenses and filters.

UNIVERSITY OF IOWA,
IOWA CITY, IOWA,
March 3, 1925.

THE ORIENTATIONS OF CRYSTALS IN ELECTRODEPOSITED METALS*

By Richard M. Bozorth

Abstract

If a metallic film is placed in the path of a circular beam of x-rays, the Debye-Scherrer circles obtained on a photographic plate will each be nearly uniform in intensity if the crystals are oriented at random. If the circles contain spots of greater intensity, certain crystal planes must be oriented so as to make an average angle α with the normal to the film. (1) A *graphical method of determining the orientations* is described, a modification of that given by Polanyi and by Uspenski and Konobejewski, together with charts of the values of α corresponding to the location of intense spots for three values of the angle β of the beam with the normal to the film, and also a table of the values for α for different planes for the cubic system. (2) *Electrodeposited films of copper, zinc and cadmium* were found to have crystals oriented at random, but *films of iron, nickel and cobalt* show special orientations. For Fe, the (111) planes tend to lie parallel to the surface; for Ni the (100) or (211) planes tend to be parallel to the surface. The orientation was less marked for Co and only slightly evident for *silver*. In the case of Ni, the degree of special orientation was found to increase with the thickness of the films studied (2 to 130×10^{-4} cm) and at the same time the size of some of the crystal grains greatly decreased, reflecting more general radiation. A magnetic field had no influence on the amount of orientation. (3) *Association of the effect with strain in the films.* It is known that electrodeposited films are in a state of stress, presumably because of the hydrogen deposited with the metal, and that strained metals tend to have oriented crystals. It is suggested, therefore, that the orientation in this case is associated with the strain developed during deposition.

1. Introduction

THE crystalline structures of rolled metals and hard-drawn wires were first explained by Polanyi, Weissenberg, Mark and Ettisch,[1] independently by Uspenski and Konobejewsky,[2] and more recently by Jeffries[3] and others. All of these observers deduced from x-ray photographs the distribution in angle of the principal crystal axes in the minute grains constituting these substances. This paper describes a

* Reported in part at the Washington Meeting of the American Physical Society, April 25, 1924. (See abstract in Phys. Rev. **23**, 764, June 1924).

[1] See especially M. Polanyi, Zeits. f. Phys. **7**, 149-180 (1921); K. Weissenberg, Ann. der Phys. (4) **69**, 409-435 (1922); M. Polanyi and K. Weissenberg, Zeits. f. techn. Phys. **4**, 199-208 (1923).

[2] N. Uspenski and S. Konobejewski, Zeits. f. Phys. **16**, 215-27 (1923).

[3] Z. Jeffries, Trans. Am. Inst. Min. Eng. **70**, 303-327 (1924).

similar study of the orientations of the crystals in electrolytically deposited metals, those examined being Fe, Co, Ni, Cu, Zn, Ag and Cd.

2. Method of X-ray Examination

The metals were examined in the form of foils. These were deposited on cathodes of polished copper or iron which, just before the deposition, were coated with a thin film of selenium, making it easy to strip the foil from the cathode for subsequent examination. The foil was now mounted in the path of a beam of x-rays of circular cross section. The x-rays were supplied by a molybdenum target water-cooled tube, run at 40 kv peak, and were filtered through a zirconia screen. The photographic plate (Eastman X-Ray 5″×7″) was placed 5 cm behind the sample, perpendicular to the incident beam.

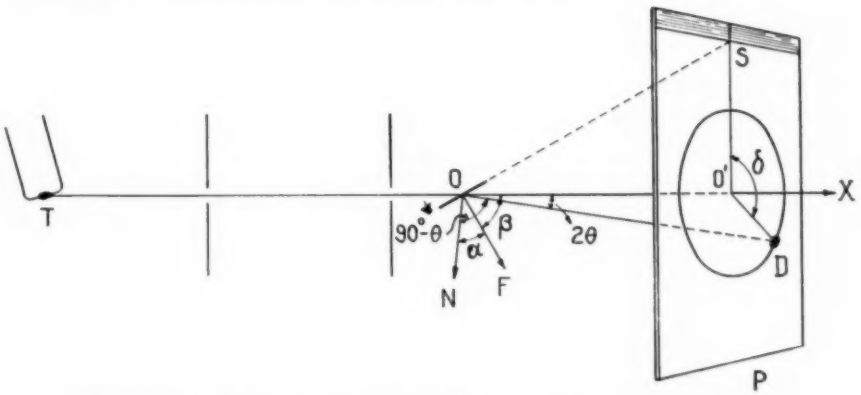


Fig. 1. Diagram showing refraction of beam to photographic plate *P*.

If the crystals in the foil were oriented at random each of the usual Debye-Scherrer circles would be of uniform intensity around its circumference except for the effect of absorption in the foil, which, in general, would be different for different directions of emergence and would produce differences of intensity between widely separated points. Regions of conspicuous intensity, such as those seen in Fig. 5, indicate, therefore, the existence of a special orientation of the individual crystals. In electrolytic foils it is to be expected that the distribution of equivalent crystallographic directions will have axial symmetry about a line perpendicular to the foil; that this is true is proved by the fact that when the foil is perpendicular to the beam each Debye-Scherrer circle is of uniform intensity around its circumference, although the consecutive circles have relative intensities greatly different from those known to correspond to random distribution.

In Fig. 1, the x-ray beam TX, cuts the sample at O and the photographic plate at O'; OF is the normal to the surface of the sample on the side from which the primary beam emerges; ON is the normal to the family of atom-planes which reflects x-rays in accordance with the equation $n\lambda = 2d \sin\theta$ on to the photographic plate P at D; the line $O'S$, chosen for reference, lies in the plane P and in the plane $O'OF$, on the opposite side of OO' from OF. The following relation[1,2] then exists between the angles marked in Fig. 1

$$\cos\alpha = \cos\beta \sin\theta + \sin\beta \cos\theta \cos\delta.$$

Of these quantities, θ is known from the crystal structure and the wavelength of the x-rays, and δ is measured on the plate; β can be determined most accurately from the relation $\tan\beta = OO'/O'S$, where OO' is calculated from the measured distances $O'D$ and the known values of θ,

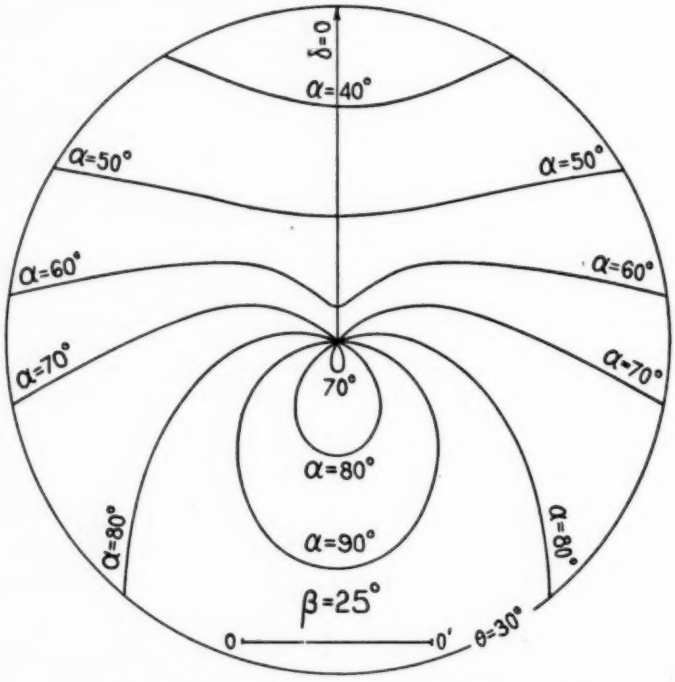


Fig. 2. Chart showing lines of constant α for $\beta = 25°$.

and $O'S$ is the distance on the plate from the central image to the edge of the unexposed streak on the plate due to the maximum absorption of scattered radiations in the plane of the sample.

In practice, the crystallographic direction [hkl] which coincides with the normal to the foil, is determined with the aid of a chart and a

table. The chart is constructed for the chosen value of β, a different chart being required for each inclination of the foil to the beam. For any arbitrary value of α a curve is drawn giving δ as a function of θ, where δ is plotted in azimuth and θ is plotted radially in such a way that a line of constant θ is a circle having the radius OO' tan 2θ, the radius of the Debye-Scherrer circle produced on the plate by x-rays reflected from crystal planes inclined at the angle θ to the incident beam (see Fig. 1). The chart is completed by drawing in a similar manner curves for other values of α chosen to facilitate interpolation, e. g. at intervals of 10°. Charts for several values of β (25°, 50°, 75°) are shown in Figs. 2, 3, and 4, and may be copied for use in determinations of this kind by so enlarging them that the length of the line labeled OO' is equal to the distance from the sample to the photographic plate.

In using a chart to determine α, the photographic plate is placed over it and values of α read off for each point of maximum intensity on each Debye-Scherrer circle. A table is now constructed giving the angles between simple planes of the same or different indices. Table I has been so constructed for the cubic system. For the Debye-Scherrer circle produced by reflection from planes whose indices are (*HKL*), the planes (*hkl*) are found for which the angles tabulated are equal to the values of α just determined. Repeating the process for the other Debye-Scherrer circles, the crystallographic plane (*hkl*) whch coincides with the plane of the foil is, in general, uniquely determined and the determination confirmed.

TABLE I

Angles between crystallographic planes in crystals of the cubic system.

(*HKL*)	(*hkl*)	Values of α, the angle between (*HKL*) and (*hkl*)				
100	100	0°	90°			
	110	45°	90°			
	111	54°44′				
	210	26°34′	63°26′	90°		
	211	35°16′	65°54′			
	221	48°11′	70°32′			
	310	18°26′	71°34′	90°		
	311	25°14′	72°27′			
	320	33°41′	56°19′	90°		
	321	36°43′	57°42′	74°30′		
110	110	0°	60°	90°		
	111	35°16′	90°			
	210	18°26′	50°46′	71°34′		
	211	30°	54°44′	73°13′	90°	
	221	19°28′	45°	76°22′	90°	
	310	26°34′	47°52′	63°26′	77° 5′	
	311	31°29′	64°46′	90°		
	320	11°19′	53°58′	66°54′	78°41′	
	321	19° 6′	40°54′	55°28′	67°48′	79° 6′

TABLE I—continued

Angles between crystallographic planes in crystals of the cubic system.

(*AKL*)	(*hkl*)	Values of α, the angle between (*HKL*) and (*hkl*)						
111	111	0°	70°32′					
	210	39°14′	75° 2′					
	211	19°28′	61°52′	90°				
	221	15°48′	54°44′	78°54′				
	310	43° 5′	68°35′					
	311	29°30′	58°31′	79°58′				
	320	61°17′	71°19′					
	321	22°12′	51°53′	72° 1′	90°			
210	210	0°	36°52′	53° 8′	66°25′	78°28′	90°	
	211	24° 6′	43° 5′	56°47′	79°29′	90°		
	221	26°34′	41°49′	53°24′	63°26′	72°39′	90°	
	310	8° 8′	58° 3′	45°	64°54′	73°34′		
	311	19°17′	47°36′	66° 8′	82°15′			
	320	7° 7′	29°45′	41°55′	60°15′	68° 9′	75°38′	82°53′
	321	17° 1′	33°13′	53°18′	61°26′	70°13′	83° 8′	90°
211	211	0°	33°33′	48°11′	60°	70°32′	80°24′	
	221	17°43′	35°16′	47° 7′	65°54′	74°12′	82°12′	
	310	25°21′	49°48′	58°55′	75° 2′	82°35′		
	311	19° 8′	42°24′	60°30′	75°45′	90°		
	320	25° 9′	37°37′	55°33′	63° 5′	83°30′		
	321	10°54′	29°12′	40°12′	49° 6′	56°56′		
		70°54′	77°24′	83°44′	90°			
221	221	0°	27°16′	38°57′	63°37′	83°37′	90°	
	310	32°31′	42°27′	58°12′	65° 4′	83°57′		
	311	25°14′	45°17′	59°50′	72°27′	84°14′		
	320	22°24′	42°18′	49°40′	68°18′	79°21′	84°42′	
	321	11°29′	27° 1′	36°42′	57°41′	63°33′	74°30′	
		79°44′	84°53′					
310	310	0°	25°51′	36°52′	53° 8′	72°33′	84°16′	
	311	17°33′	40°17′	55° 6′	67°35′	79° 1′	90°	
	320	15°15′	37°52′	52° 8′	74°45′	84°58′		
	321	21°37′	32°19′	40°29′	47°28′	53°44′	59°32′	
		65°	75°19′	85° 9′	90°			
311	311	0°	35° 6′	50°29′	62°58′	84°47′		
	320	23° 6′	41°11′	54°10′	65°17′	75°28′	85°12′	
	321	14°46′	36°19′	49°52′	61° 5′	71°12′	80°44′	
320	320	0°	22°37′	46°11′	62°31′	67°23′	72° 5′	90°
	321	15°30′	27°11′	35°23′	48° 9′	53°37′	58°45′	63°36′
		72°45′	77° 9′	85°45′	90°			
321	321	0°	21°47′	31°	38°13′	44°25′	50°	60°
		64°37′	69° 4′	73°24′	81°47′	85°54′		

The pattern due to an electrolytic foil of nickel, reproduced in Fig. 5A, may serve to illustrate the method. For this photograph β was made 50°. The values of α found from the chart are given in the second column of Table II; the values taken from Table I for (*hkl*) = (211) are given in the third column and this is the only value of (*hkl*) which gives even approximate agreement between columns 2 and 3. It will be noted that column 3 contains one value not found in column 2 but it is easy

to show that under the limitations imposed upon β and θ the corresponding reflection cannot occur.

TABLE II

Reflecting planes $n(HKL)$	α(obs.)	α[for $(hkl)=(211)$]
(111)	61°, 90°	19°28′, 61°52′, 90°
2(100)	36°, 66°	35°16′, 65°54′
2(110)	30°, 55°, 73°, 90°	30°, 54°44′, 73°13′, 90°

A second method of determining the plane (hkl) which coincides with the foil surface, was used in a few cases. This consisted in mounting the foil on a photographic spectrometer of the Bragg type, with the foil surface in place of the usual single crystal face. The foil was rotated with uniform angular velocity, and a screen containing an aperture, corresponding to the ionization chamber slit in the Bragg

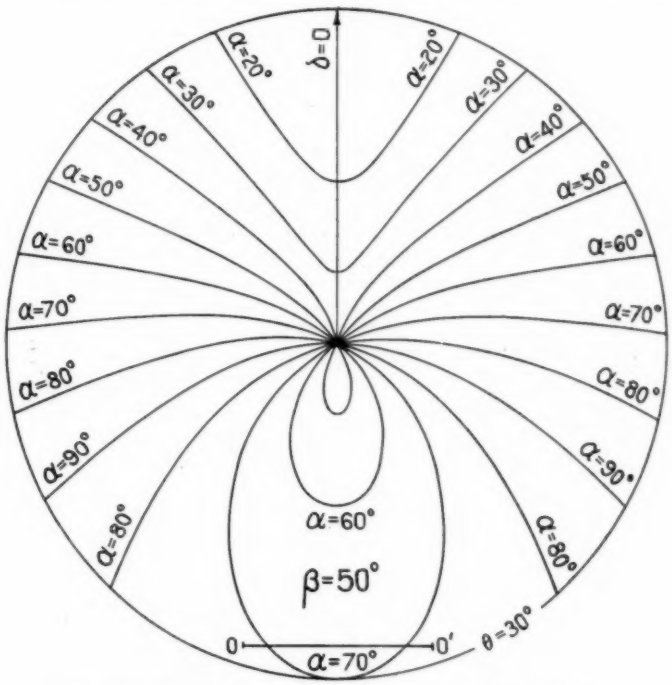


Fig. 3. Chart showing lines of constant α for $\beta=50°$.

spectrometer but 10° in width, was rotated with just twice this angular velocity. With this arrangement no planes can reflect x-rays on to the photographic plate except those lying very nearly in the plane of the foil. The photographs taken in this manner resemble closely those

taken with a single crystal. This method gave results confirming in every case those of the first method described. The second metnod, while it has certain advantages, is open to the objection that it does not permit a satisfactory estimate of the degree of special orientation, such as can readily be derived from the appearance of the diffraction patterns obtained in the first method.

3. Experimental Results

Electrolytic films of Fe, Co, Ni, Cu, Zn, Ag and Cd, deposited under various conditions, were examined with x-rays in the ways described above. Table III gives a summary of the results obtained. All deposits, unless otherwise stated were made on copper at room temperature with a current density of 0.005 amp./cm^2, and were 0.003 cm thick.

Table III

Metal	*Solution*	*Special orientation*
Fe	$FeSO_4$, 0.7m; NH_4Cl, 0.8m; $P_A = 5.0$; 50°C; current density 0.050 amp./cm^2	(111) strong
Co	$CoSO_4$, 1.0m; saturated with H_3BO_3	Not determined, medium weak
Ni	$NiCl_2$, 0.1m; $NiSO_4$ 0.9m; H_3BO_3 0.6m; acid with H_2SO_4, P_A varied from 3.5 to 6.1; 40°C	(100) strong
Ni	$NiCl_2$, 0.9m; $NiSO_4$ 0.1m; H_3BO_3 0.6m; acid with H_2SO_4, $P_A = 3.0$	(211) strong
Ni	$NiCl_2$, 1.0m; $P_A = 4.0$	None
Cu	$CuSO_4$, 1.0m; H_2SO_4, 0.7m	None
Zn	Alkaline cyanide, Zn 0.5m, 40°C	None
Ag	Alkaline cyanide, Ag 0.2m	None
Cd	Alkaline cyanide, Cd 0.1m, 40°C	None

The effects of some of the different factors involved in deposition were investigated for the case of nickel. An interesting effect was observed when different thicknesses of this metal were plated from the same bath with the current density and other factors as nearly as possible the same, i. e., varying only the time of deposit. Photographs were taken using foils of thicknesses 2, 12, 23, 55 and 130 $\times$ 10^{-4} cm. The third and the last of these are reproduced in Figs. 5B and 5C, respectively. The photograph (not reproduced) taken with the thinnest foil shows no appreciable degree of special orientation. Fig. 5B shows that in the middle foil of the series the special orientation is appreciable, while Fig. 5C shows that in the thickest foil the crystals exhibit a decided tendency to become oriented so that their (100) planes are parallel to the surface of the foil. The photographs show, besides orientation effects, an increasing amount of x-radiation reflected on to the plate inside of the first Debye-Scherrer circle. This is general

radiation[4] of wave-lengths in the region 0.30 to 0.50A, and its increasing prominence is due[5] to the fact that in increasing proportion the thicker foils are composed of very minute crystals, with dimensions of the order of 10A. Fig. 5D shows the diffraction pattern obtained from the later-deposited half of the thickest foil, the first-deposited half having been etched away with nitric acid. This pattern compared with that for the entire foil (Fig. 7) shows weaker diffraction effects due to fine crystals, and shows a higher degree of special orientation than any of the other patterns.

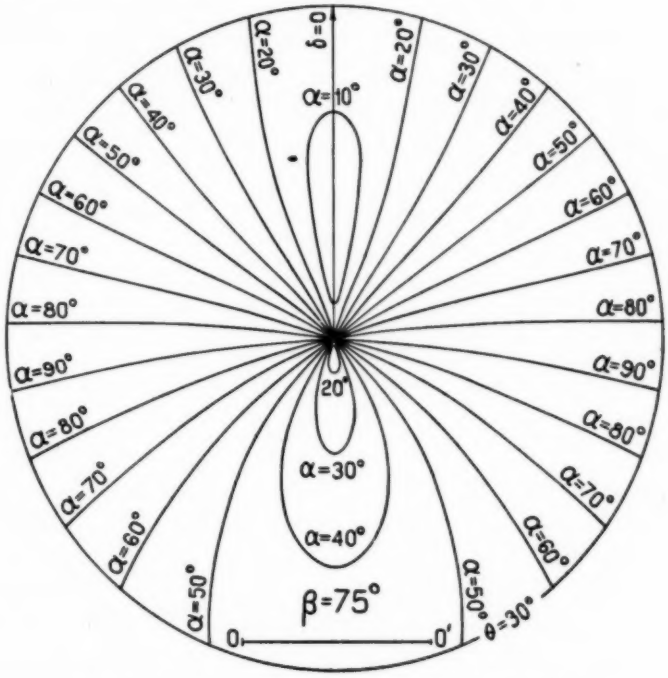


Fig. 4. Chart showing lines of constant α for $\beta = 75°$

Some experiments were performed in which Fe, Ni and Cu were deposited in magnetic fields having various strengths and various directions with respect to the surface of the cathode. Other experiments were made using an inert (Pt) anode. Although these modifications seemed at first to change the degree or kind of crystal orientation in Ni, the effects were later traced to changes taking place in the solutions.

[4] R. M. Bozorth, J.O.S.A. and R.S.I. **9**, 123-127 (1924).
[5] Zsigmondy, Kolloidchemie, 3d ed. (1920), pp. 394, 403-5.

4. Discussion of the Results

The experiments described above show that some metals, when deposited electrolytically from solution, tend to form crystals oriented in a definite way with respect to the cathode surface. This tendency is greater in iron and nickel than in any of the other metals investigated. It is evident, however, in cobalt and silver. Preliminary experiments show that the degree and kind of special orientations are influenced to some extent by the composition of the solutions from which the metals are deposited.[6] Results already obtained support the belief that the special orientations are intimately connected with the state of stress which exists in the deposited metal. Kohlschütter and Vuilleumier[7] have shown that deposits of Fe, Ni and Ag, as usually produced, are in a state of tension, and experiments performed in this laboratory yield quantitatively the values of these tensions for different thicknesses of iron deposit. Also, Polanyi[8] has shown that the tension produced in metals by working produces special orientations of their crystals, and he has given an explanation for the production of such orientations. A natural explanation for the observed orientations in electrolytic foils is, then, that the tension known to be present in such foils produces orientations of the crystal grains in a way similar to that in which orientations are produced in hard drawn wires or rolled sheets. In this connection it is significant that the metals Fe and Ni, which are deposited in a state of tension and with special orientations of their crystals, are much harder mechanically than Cu, Zn and Cd in which the crystals are orientated approximately at random.

The cause of the tension which exists in the metals Fe, Co and Ni, and the manner in which this tension produces the crystal orientations, have yet to be considered. Experiments with Ni, however, indicate that a necessary factor in producing the tension is the hydrogen which is deposited along with the metal; in fact Kohlschütter and Vuilleumier[7] have shown that hydrogen electro deposited upon a thin nickel deposit produces in it a marked expansion, which disappears when the circuit is broken. On this basis the following mechanism is suggested for the production of the stresses in the deposits. The hydrogen which is deposited with each "layer" of metal causes the metal atoms to be laid down somewhat farther apart than they normally

[6] This is also the conclusion of R. Glocker and E. Kaupp from their work described in Zeits. f. Phys. **24**, 121-139 (May 22, 1924).

[7] V. Kohlschütter and E. Vuilleumier, Zeit. f. Elektrochem. **24**, 300-321 (1918).

[8] M. Polanyi, Zeits f. Phys. **17**, 42-53 (1923).

are in crystals of the pure metal. As successive layers are added, however, the forces which held the hydrogen in the deeper layers while they were being deposited, no longer exist, and the hydrogen diffuses out of the metal leaving it in a state of tension. Since this process

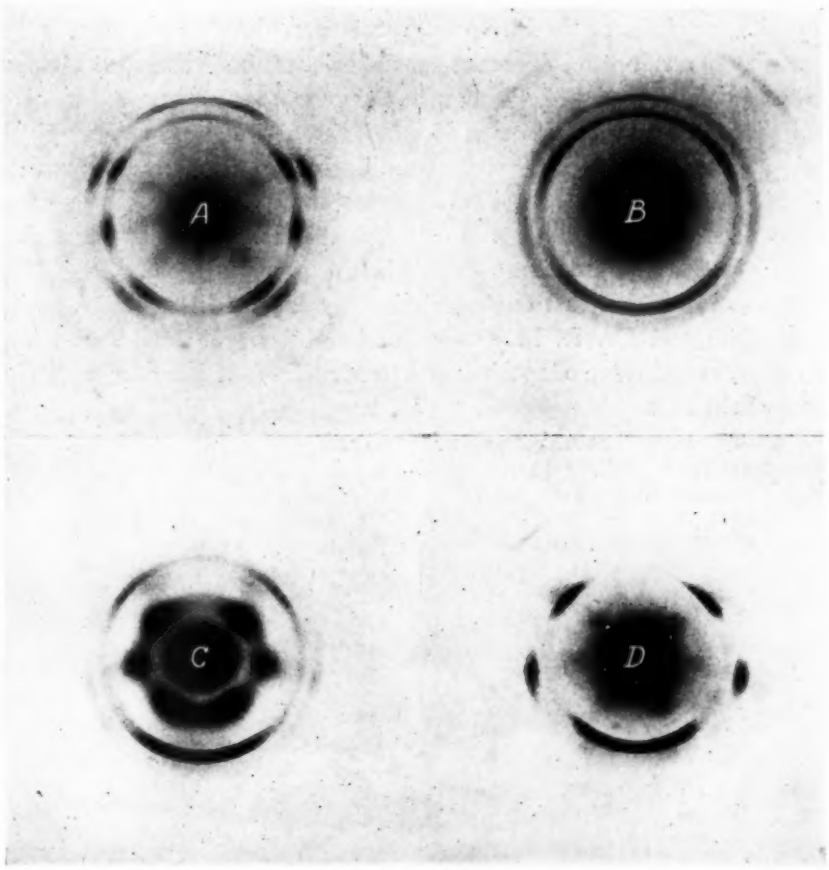


Fig. 5. X-ray photographs obtained with electrodeposited foils of nickel.
A. $\beta = 50°$, $(hkl) = (211)$. B. Thickness 23×10^{-4}cm.
C. Thickness 130×10^{-4} cm. C. Thick foil, later deposited half.

goes on continually during deposition the difference between the stresses in the innermost and outermost layers increases, and the compressive stress in the layer next to the cathode becomes greater and greater (but not, of course, in proportion to the thickness of the deposit.) The compressive stress in the layers first deposited may attain such a magnitude that some of the crystals are crushed, forming new crystals so fine that the reflection of x-rays by the metal is modified in a char-

acteristic way as seen in Fig. 5C and previously discussed. On the other hand, in the other layers where the crystals are formed under greater tension the orientations should be more marked, as was found to be the case.

It will be noted that the metals giving the most severely strained deposits are those of the iron group. Silver, which follows these in the intensity of strains and degree of special orientation is the next element following palladium. McKeehan has shown[9] that the space-lattice of palladium is expanded when it is made the cathode of an electrolytic cell producing hydrogen, and that the lattice again contracts upon the loss of hydrogen. The effects here discussed emphasize again the often-noted anomalies, magnetic and otherwise, associated with the eighth group elements and their neighbors in the periodic table.

In conclusion I wish to acknowledge my indebtedness to Dr. L. W. McKeehan and Dr. R. M. Burns for helpful discussions concerning the structure of electrodeposits, and to Mr. C. W. Warner for preparing some of the foils.

BELL TELEPHONE LABORATORIES, INCORPORATED,
NEW YORK, N.Y.,
June 1, 1925.

[9] L. W. McKeehan. Phys. Rev. (2) **21**. 334-342 (1923).

BINAURAL BEATS

By C. E. Lane

Abstract

By introducing a tone of frequency f into one ear and another tone of frequency $f+N$ into the opposite ear, where N is less than 5 or 6 cycles, two kinds of binaural beats are obtained. *Objective binaural beats* are heard for most values of f within the audible frequency range, provided there is the proper difference in amplitude between the two tones. For telephone receivers as sound sources, this difference for best beats is about 55 TU and for the same receivers supplied with sponge-rubber cushions about 62 TU. These beats are heard because the louder tone is conducted through the head to the ear of the weaker tone and the two tones there are about equally loud. *Subjective binaural beats* are heard for frequencies below 800 or 1000 cycles when the tones at the two ears have about the same amplitudes, differing by not more than 25 TU. Data obtained with 22 observers are summarized. The evidence indicates that these beats are not due to cross conduction but are of central origin and the result of the sense of binaural localization of sound by phase. If the beats are slow (less than 1 per sec.) they are generally recognized as an alternate right and left localization, though some observers may report one or more intensity maxima during the beat cycle. Such maxima are explained as the result of one's interpreting the sound as louder when localization is more definite. Fast beats (more than 1 per sec.) are generally recognized as an intensity fluctuation. They are explained by assuming that the sound appears louder when the phase relations are such that it is normally best localized in the position toward which the attention is directed. This explanation is supported by observations made with a constant source rotating around the head of a listener.

Introduction

THIS paper is concerned with experiments undertaken to determine the nature of "binaural beats." Binaural beats of one kind have been described by G. W. Stewart[1] and others. Binaural beats of another kind were observed by R. L. Wegel and the writer[2] in making measurements of binaural masking. That the nature of these two kinds of beats was different was not appreciated until the investigation reported here was begun. In the work of Wegel and Lane the beats were investigated only sufficiently to show that their existence did not invalidate any conclusions proposed concerning the mechanism of hearing.

[1] G. W. Stewart, Phys. Rev. **9**, pp. 502, 509, 514 (June 1917).
[2] R. L. Wegel and C. E. Lane, Phys. Rev. **23**, (March 1924).

We shall use the "transmission unit"[3] recently adopted by the Bell Telephone System. Taking for each frequency the threshold value as the unit of a geometrical scale, the magnitude of any tone in transmission units is numerically equal to ten times the common logarithm of the ratio of the intensity of the tone in the ear canal to the threshold intensity. If a tone is of such an intensity that the rate at which sound energy enters the ear is ten times that required for minimum audibility the magnitude of the tone is said to be 10 TU, if 100 times 20 TU, etc.

As an illustration of the phenomenon of binaural beats, it may be stated that if, by means of telephone receivers, two tones of 250 and 251 cycles are introduced into opposite ears, and if the intensity of the first or primary tone is kept constant at 80 TU above threshold while the intensity of the other or secondary tone is gradually increased, starting at zero, the sensations produced are as follows: Nothing but the steady primary tone is heard until the secondary reaches a value of 5 or 10 TU when very faint beats or intensity fluctuations become perceptible. These beats gradually become more intense until at about 25 or 30 TU they are loudest. For a further increase in the intensity of the secondary tone the beats gradually become fainter and at about 45 or 50 TU disappear. When the intensity of the secondary tone is increased to 60 TU, beats again are heard. However, these beats differ in many ways from those first observed. When the intensity of the secondary tone reaches about 80 TU, or when the two tones are equally loud, these new beats are heard best. They disappear when the intensity of the secondary tone reaches about 100 TU.

The nature of the beats and the range of relative intensities for best beats depend somewhat upon the frequency of the beating tones, the frequency of the beat, and the manner in which the sounds are introduced into the ears. The beats that are heard best when the tones are greatly different in intensity are designated objective beats and those that are heard best when the tones are equally loud, subjective beats. The reason for this terminology will appear later.

[3] The difference S in TU (transmission units) between two tones of the same frequency is defined by $S = 10 \log_{10} (I_1/I_2)$ where I_1 and I_2 are their respective intensities. See the following papers:

H. Fletcher, Jour. Franklin Inst. (Sept. 1923).
H. Fletcher, Phys. Rev. **23,** 427 (March 1924).
Martin and Fletcher, Jour. A. I. E. E. (March 1924).
W. H. Martin, Bell Tech. Jour. (July 1924).
Fletcher and Steinberg, Phys. Rev. **24,** 306 (Sept. 1924).
R. V. L. Hartley, The Electrician (Jan. 16 and 23, 1925).

Apparatus and Method

The apparatus was essentially the same as previously used in this laboratory in the determination of the frequency sensitivity of normal ears[4] and the auditory masking of one tone by another.[2] Telephone receivers were used as sound sources. The currents at different frequencies were supplied by means of vacuum tube oscillators equipped with filters to eliminate effects due to harmonics. Two voltage attenuators were used, one associated with each receiver. In taking the data on objective beats, minimum audibility was separately determined for each receiver on the same ear. The primary tone was then adjusted to 80 TU above minimum audibility and the receiver transferred to the opposite ear. Then with the receiver supplying the secondary tone on the first ear, its output was adjusted until best beats were heard.

For taking the data on subjective beats, minimum audibility was again determined for each receiver on the same ear. The tone from both receivers was then adjusted to the same level above minimum audibility and one tone presented to each ear. In order to determine the phase relation at any time between the tones from the two receivers, an auxiliary receiver was connected through an amplifier across the input of the two attenuators. By listening to this receiver, a second observer could at any time report the phase relations.

Objective Beats

1. *The relative intensities of the two tones for hearing objective beats.* The difference in TU between tones for best hearing objective beats was obtained first without and then with rubber cushions between the ear and the receiver cap. The observed values are given in Table I. A deviation of 20 or 25 TU on either side of the values given usually resulted in the disappearance of the beats. The table presents data for two different observers, both of normal hearing. The frequencies of the primary tones used are given in the first column. In taking the data the secondary tone differed from the primary by about one cycle. Three successive determinations of the difference between the two tones for best beats were made for each frequency. The averages of the values thus obtained are shown. The agreement between the two observers is very satisfactory. It is seen that the addition of rubber cushions has increased the intensity difference for hearing best beats about 7.0 TU.

2. *Theory of objective beats.* In monaural hearing where the two tones are introduced into the same ear, beats are heard best when the magnitudes of the two tones are equal, and beats cannot be heard at all if

[4] Fletcher and Wegel, Phys. Rev. **19**, 553 (June 1922).

the tones differ by more than about 30 TU. The data below give as the average difference for best hearing the objective binaural beats, a value of about 55 TU when using receivers without cushions and 62 TU with the cushions. In consideration of these facts, there seems to be only one possible explanation for the hearing of objective binaural beats. The beats evidently originate in the ear of the weaker tone, the louder tone being conducted across the head to this ear where interference takes place. When the magnitudes of the two tones are adjusted for best beats their difference corresponds approximately to the difference in sound energy of the louder tone at the two ears.

TABLE I

Difference between tones for best beats

f	Without cushions (C.E.L.)	Without cushions (A.G.)	With cushions (C.E.L.)	With cushions (A.G.)
200	54 TU	48 TU	67 TU	54 TU
300	61	44	68	55
400	57	64	64	66
600	49	61	66	70
1000	47	50	49	57
1500	42	49	47	59
2000	50	57	52	61
3000	63	62	67	62
4000	69	69	75	72
Average	54.7	55.5	61.7	61.4

Measurements of the difference between the response of an ear to a tone introduced into it by means of a telephone receiver and the response of this ear to the same tone when introduced into the opposite ear have been determined by two other independent methods. The data were taken for the same range of frequencies as shown in Table I. In the first method it was found for a person entirely deaf in one ear that the average difference in intensity required for minimum audibility between a tone in the good ear and in the bad ear was about 58 TU. In the second method it was found that for a loud tone of one frequency to just mask a faint tone of another frequency the loud tone must on the average be about 56 TU louder when presented to the ear opposite the faint tone than when presented to the same ear.[2] These values agree well with the values of 55.5 TU and 54.7 TU as determined by the beat method.

3. *Sound conduction from one ear to the other.* There are four ways in which a tone introduced into one ear may get across to the opposite ear.[5] First, it may pass around the head through the air. Second, if

[5] It is assumed that the receivers at each ear are not joined mechanically as by a head band.

the sound source is held against the ear, the vibrations in it may be communicated directly to the flesh and bones of the head and thence across. Third, the varying air pressure at the ear causes the bones of the inner ear and the other surrounding bones to vibrate even though the sound source may not be directly in contact with the head. In this way sound likewise reaches the remote ear by bone conduction. Fourth, the motion of the ear drum of the proximal ear may transmit air waves through the Eustachian tubes to the opposite ear.

If the sound source is not held against the ear, in most cases the greatest part of the sound reaching the opposite ear arrives there by air-conduction around the head. If the sound source is held against he ear as in the case of telephone receivers, most of the sound reaching the remote ear arrives there by bone-conduction and is the result of direct communication to the head of vibrations in the receiver cap. This conclusion was reached after trying the following experiment. The external meatus of the ear into which the louder tone is introduced was plugged and the receiver on the other ear covered by heavy layers of sound absorbent material. The relative intensities of the two tones for best beats was found to be the same as before. No satisfactory way has yet been found for determining the effectiveness of the other two paths in conducting sound across the head.

Since the purpose of this investigation was to explain the beats rather than to make an exact determination of the difference between the primary and secondary tones for best beats for an average observer using average receivers, no large amount of data was taken. However, the data obtained show that, while the difference for best beats as determined for some one primary frequency may vary as much as 10 or 15 TU for the same observer using different receivers or for different observers using the same receivers, the averages of the differences as determined for a range of frequencies between 200 and 4000 cycles is nearly independent of both observers and receivers, provided the receivers are not radically different. The irregular variation of the data with frequency is primarily the result of the complex path by which the primary tone reaches the remote ear, and the variations for the same frequency for different observers or different receivers are the result of small changes in the various elements constituting this path.

4. *Localization of objective beats.* In connection with the hearing of objective beats it was observed that the beats are generally localized in the ear of the louder tone. This, however, is not an argument against the explanation already given which states that they are actually due

to interference in the other ear. Localization of the varying stimulus is one thing and the recognition of its existence is another. The remarkable independence of the two ears enables one to hear weak beats in one ear in the presence of a very loud tone in the other, but this loud tone so holds the attention that one locates the beats as coming from the latter ear. It should be added that localization of the beats in the ear of the louder tone does not always occur. Two observers who first localized them in this ear, later, after a little practice, best localized them either in the other ear or somewhere between the ears.

A phenomenon similar to this has been observed in listening to two tones quite different in frequency. If one of these tones is presented to one ear it is localized in that ear, but if a much louder tone of another frequency is at the same time presented to the opposite ear the localization of the first tone may be shifted somewhat though the tone still remains distinctly audible.

Subjective Beats

1. *The effect of varying the beat frequency of subjective beats.* As stated above subjective beats are those heard best when the tones are equally loud. Data for the determination of the effect of varying the beat frequency of these beats were taken for 22 observers. Most of the observers had no preconceived notion as to what they were going to hear and care was taken to offer no suggestions that would influence them in the interpretation of their sensations. The frequencies used were 250 and $250+N$ cycles where N was the beat frequency. N was varied for most of the observers from 1/4 to 4 cycles. For the sake of simplicity in recording the data, the higher frequency was always presented to the right ear. Receivers supplied with the sponge-rubber cushions were used. However, preliminary tests showed that the character of subjective beats heard was unaltered by the use of receivers without cushions or by the presentation of the tones to the ears through rubber tubes.

We will first consider the experiences of the 22 observers while listening to slow beats, meaning by slow beats those having periods of more than one second. Four of them reported hearing nothing but a steady tone of rather indefinite localization somewhere within the head. The other 18 recognized the beat period by an alternate right and left localization, the sound being best localized on the side of the tone leading in phase. Their experiences, however, during the time of transitions of localization from one side of the head to the other differed.

Three of them reported no sense of motion but simply an alternate rising and falling of intensities at the two ears, the sound being equally loud at the two ears at the time of agreement and opposition of phase. Seven described the localization as passing along a path either just outside or inside the front or top part of the head during phase agreement and through the lower or back part during opposition, the latter path being less definite than the former. One observer at one time reported the sound as passing back of the head during agreement in phase and at another time in front. In both cases the sound passed straight through the head from one ear to the other during opposition in phase. Two observers reported the sound as passing from left to right and right to left along the same path. For one, this path was through the back of the head and for the other directly between the ears. One described the sound as traveling in a horizontal circle outside the head and at a distance, passing in front during phase agreement and in back during opposition. Another reported the sound as traveling in a circle outside the head. However, in this case the circle lay entirely back of the head. One observer reported the localization as passing through the back of the head at the time of opposition of phase and a period of no localization during phase agreement. Still another reported definite localization in front part of the head during agreement in phase and no localization during opposition. The last of the observers experienced a sensation of motion but was not able to assign any definite path to it.

The reports of the observers as to intensity maxima for the slow beats were as follows. Four reported no maxima. Three reported a maximum at the time of phase agreement located in the front part of the head. One at first reported a maximum at the time of phase agreement but later reported it just before opposition in phase and located in the right ear. Three observers reported a maximum in the right ear just before opposition in phase. Six reported two maxima, one in each ear shortly before and shortly after opposition in phase. The other observer most of the time reported a maximum at each ear but on two occasions reported a primary maximum in the top of the head at the time of phase agreement in addition to the two secondary at each ear.

All but four of the observers who listened to the slow beats listened to beats of intermediate and fast frequencies. Intermediate refers to beats from one to two times per second and fast to beats occurring more than twice per second. Of the 18, four were not able to report the beta frequency for the intermediate beats. Six described an intensity fluctuation inside the head of rather indefinite localization accompanied by a

rather vague sense of motion. Four described an intensity fluctuation within the head of the same frequency of the beat accompanied by a sensation of sound localization describing a circle above the head but with only half the beat frequency. Three reported the sound localization as describing a circle above the head corresponding to the beat frequency. The last described the sound as shooting through the head from left to right at the time of phase agreement.

As to the existence of intensity maxima for intermediate beats, only about half of the observers were able to satisfactorily report the time at which such maxima occurred. Most of these reported the maxima as occurring either at 0° phase difference or at about 120° phase difference. Some changed from one of these phase relations to the other during the course of the experiment.

All of the observers who listened to fast beats could notice an intensity fluctuation but two or three were not able at any time to report the beat frequency. Some could report the beat frequency only part of the time. Only one of the observers reported any sensation of motion.

It should be added here that the experiences of all the observers while listening to subjective beats were very indefinite and difficult for them to describe. Their reports were in some cases more inconsistent than the preceding data might indicate. Several observers at times spoke of periodic changes in quality that assisted in the recognition of the beat, but were not able to define the nature of the change. The data as given are in agreement with the observers' most consistent reports of their experiences.

2. *Effect of varying the frequency of the beating tones.* Data were also taken to determine the effect of increasing the frequency of the tones producing subjective beats. Seven observers who could follow the beats at 250 cycles with the least difficulty were used. The beat frequency was kept constant at one beat per second. All were able to hear the beats for frequencies as high as 600 cycles, only two as high as 800, and only one as high as 1,000. For frequencies higher than 1,000 cycles none were able to hear the beats.

3. *The range of relative amplitude for hearing subjective beats.* Data were taken for a few observers to determine the range of relative intensities over which subjective beats are audible. The limiting difference between the two tones for hearing the beats was found to be somewhere between 20 and 25 TU. Thus the breadth of the range of relative intensities for hearing subjective beats is about the same as it is for objective binaural beats. Therefore, when the attenuation of sound

in passing through the head is greater than 40 or 50 TU there should in general be a range of relative intensities between the ranges for hearing objective beats and subjective beats for which no beats are audible. Such is found to be the case.

4. *Summary of essential facts.* The following are the essential facts revealed by the data on subjective beats:

(a) If two tones of equal intensities and nearly the same frequencies are simultaneously presented to opposite ears, the beat frequency can be recognized by about 80 percent of the observers provided the frequencies of the beating tones are less than 800 or 1000 cycles. For higher frequencies the beats cannot be heard.

(b) If the beats are slow, the one outstanding phenomena observed by all who recognized the beat is an alternate left and right localization of the sound, localization being on the side of the tone leading in phase.

(c) Most observers who hear the slow beats experience a more or less vague notion of the localization traveling along some path through the median plane when the localization shifts from one side of the head to the other, but there is no good agreement among the observers as to the position of this path.

(d) The passing of the localization through the median plane is generally more clearly defined during phase agreement than during phase opposition.

(e) While all observers who heard the slow beats, reported without any previous suggestions the existence of the alternate right and left localization, none reported any intensity maxima until questioned as to the existence of such maxima. However, when questioned, over 80 percent of the observers reported maxima corresponding to one or more of the following three phase relations: (1) phase agreement, (2) 30° or 40° before opposition and (3) 30° or 40° after opposition. There was no good agreement among the observers and several during the course of the experiments shifted from one phase relation to another in their report on the time of intensity maxima.

(f) For fast beats the chief sensation is that of an intensity fluctuation of the sound located somewhere within the head.

(g) For intermediate beats some reported a predominating sensation of motion, others of intensity fluctuation and still others seemed to experience both sensations about equally well and could direct their attention upon either at the sacrifice of the other.

(h) Subjective beats are heard equally well for tones introduced into the ears by means of telephone receivers with and without receiver cushions or presented by means of rubber tubes.

(i) So long as the two tones are of equal intensity, the hearing of subjective beats is independent of their loudness.

6. *Theory of subjective beats.* Most writers on the subject of binaural localization of sound agree that such localization for low frequencies is the result of direct perception of the phase difference at the ears. This means that the vibratory character of the sound does not terminate at the end organ but is in some form transmitted to the brain. This sense is not highly developed and generally exists only for frequencies below 700 or 800 cycles. The theory advanced here for subjective beats attributes the hearing both of the right and left effects observed and of all intensity maxima to the sense of binaural localization and, therefore, places the origin of these beats in the brain.

Stewart has offered a very complete cross-conduction theory for explaining the binaural beats here called subjective, but at the same time has recognized that many good arguments may be advanced against such a theory. In consideration of the facts presented on the preceding pages there are several reasons why some theory not based on peripheral interference should be used for explaining these beats. First, the attenuation of the sound in passing through the head is far too great to permit perceptible amplitude fluctuations at the ears when the tones there are equally loud. Data on monaural hearing show that one cannot detect variations at the ear that are less than .5 TU whereas a cross-conduction theory requires the perception of variations of the magnitude of .03 TU to .003 TU or even less. Second, if cross-conduction were responsible for the hearing of these beats, their clearness should, in some way, depend upon the amount of cross-conduction. The use of different sound sources for which there are known differences in the amount of cross-conduction shows that such is not the case. Third, if the subjective beats were due to cross-conduction, the hearing of them should not be limited to frequencies for which binaural localization by phase is possible. Fourth, there is a range of amplitude ratios for which beats cannot be heard which is between the range for hearing the subjective beats and the range for hearing the objective beats. If the beats were all caused by cross-conduction, they could be heard over the entire range.

There are many reasons for believing that binaural subjective beats are the result of binaural localization by phase. These beats can only

be heard for frequencies that can be localized by phase. When the beats are slow, the chief phenomenon observed is that of wandering localization. When intensity maxima are indicated, they are associated with positions of best localization, as localization in the median plane or at the two ears. It is not surprising that the sound should be considered louder by most observers at the time of best localization for the mind can best attend it then. The sound is generally localized in the median plane at the time of phase agreement, but the localization in this plane is different for different observers. This is as it should be, for the position of a sound cannot be localized in the median plane by phase alone. The uncertainty of localization and lack of agreement among observers for phase differences in the neighborhood of 180° are likewise to be expected. Observers are then listening to phase relations with which they have never learned to associate positions.[6] The experiences reported, therefore, depend upon the psychological reaction of the observers to an entirely new phenomenon.

When the beat frequencies are fast the nature of the mind makes it impossible to follow the sound in any wandering path of localization. The attention would have to move from one position to another entirely to fast. As a result the attention is centered on some definite localization and the sound appears louder when the phase relations are such that the sound is best localized in this position. The beats then are not intensity fluctuations in the ordinary sense, but rather rapidly recurring conditions for definite localization.

At intermediate beat frequencies one may be able to recognize that the localization of the sound is wandering when the frequency is too fast to follow in its path of localization. This accounts for the fact that the correct frequency of the beats is not given if one reports it from the apparent period of wandering localization. However, if attention is only directed upon apparent intensity fluctuations for one position of localization, beats of the correct frequencies are heard for the same reason as that given for hearing the fast beats.

Additional plausibility is given to the explanation offered above for subjective beats by the results of the following experiment: A receiver emitting a pure tone was caused to describe a circle in a horizontal plane about the head of an observer in a large room with non-reflecting walls. When the receiver moved slowly it was observed to pass from left to right and back again with little or no intensity variation of the tone.

[6] R. V. L. Hartley and T. C. Fry, Phys. Rev. **18**, 431 (Dec. 1921).

However, when the receiver made three or more revolutions per second one was not aware of any motion of the sound source but an apparent intensity fluctuation corresponding in frequency to the number of revolutions was observed.

BELL TELEPHONE LABORATORIES, INCORPORATED,
NEW YORK CITY.
May 7, 1925

BOOK REVIEWS

The New Theories of Matter and the Atom. ALFRED BERTHOUD. Translated from the French by Eden and Cedar Paul.—The great advances which have been made in recent years in the field covered by this book have fascinated the scientific mind and created a desire among intelligent men to acquire some understanding of the new developments. This desire is properly being met by the appearance of a considerable number of books on the subject written in a non-technical style. The work under review is a somewhat more advanced type of this kind of book. The ideas which have prevailed regarding the nature of matter are developed for the most part in chronological order, and a very good account is given of the current theories. Its style makes the book very readable. In a field where there is at present so much speculation it is difficult to present matters so that the reader will always clearly understand the extent to which the different ideas are generally held. The author, for example, accepts the numerical equivalence of mass and energy and uses it in a number of calculations throughout the book without pointing out that this equivalence is held to be more speculative than other portions presented. Michelson alone is given the credit for the Michelson-Morley experiment. The misspelling of Michelson's name throughout the book is unfortunate. Ramsay and Soddy, instead of Rutherford and Soddy, are credited with the theory of atomic disintegration. It is stated that incandescent substances give off electrons when exposed either to x-rays or to ultraviolet light, whereas these agents are not necessary. It is a sign of the rapid progress in science that, contrary to statements made in this book, there is no longer a haitus between infrared and Hertzian waves, and x-rays are now known to be refrangible. The French term milliard is used throughout, although in America, at least, we have an English equivalent. The book is to be highly recommended to those desiring an authentic account of this all-important subject. Pp. 259. The Macmillan Company, New York, 1924. $3.50. JOHN ZELENY

Foundations of the Universe. M. LUCKIESH.—This book is one of a series of volumes issued under the title of *Library of Modern Sciences*. It appears to be the object of this series to give the present state of knowledge in various fields in language that is not technical and in a form to make the reading interesting to the general reader. The author of the volume under review starts out with the statement that knowledge of the physical world has been the foundation of civilization and he emphasizes throughout man's relation to the physical universe and his limitations in attempting to understand it fully. The whole treatment is along very broad lines. There is no attempt at a systematic treatment and yet there is system in it. A chapter on men, atoms, and stars is followed by chapters on matter and motion, and on molecular motion. Then follow chapters on the nature of light, what is space, the velocity of light, and the epoch of Einstein. These are followed by portions on the elements of matter, the electron theory, and the evolution of the elements. Next we come to, inside the atom, the quantum of energy and atomic structure. The treatment proper closes with a philosophical chapter on the fateful unknown, at the end of which are some speculations on the existence of an omnipresent Mind that is at the bottom of things. A chapter on the growth of knowledge gives an interesting list of great names in the physical sciences arranged chronologically and stating in a few words what each chiefly contributed. A final chapter gives a table of

important units and magnitudes. As is seen from the contents, the author has stressed those parts of physics which have been receiving most attention in recent years and these parts comprise the foundations of the Science. The general reader must not expect to acquire a deep comprehension of the field treated by reading a popular book like this but he will at least have had a vision showing him what it is all about, and will have found food for much thought.—Pp. viii+245. D. Van Nostrand Company, New York. 1925. $3.00. JOHN ZELENY

Die Grundlage der Macschen Philosophie. HUGO DINGLER.—In this little book of 106 pages the author gives at first with greatest sympathy and admiration, a short biography of Mach. He then proceeds to Mach's general attitude toward the problems of physics, philosophy, and physiology. Mach himself rejects the title of a philosopher; he considers himself merely as a philosophic dilettant (*philosophischer Spaziergänger*). Grown up in close and sympathetic contact with nature, Mach was a collecting scientist, a quiet and unassuming investigator, who tried to go to the bottom of things. Kant's problem of knowledge or epistomology had a decisive influence on Mach's thinking; nevertheless, Mach tried to eliminate all metaphysical elements from physics and especially the "thing in itself." This tendency led Mach to reject the atomic theories in physics and chemistry and, finally, the theory of relativity, even though some of his criticisms of Newton's dynamics led half a century later to that general theory. Mach calls the last principles of science instinctive, and his instinctive knowledge is not very different from Kant's a priori knowledge.

Mach wanted to arrive at a theory of knowledge on the basis of physical sciences by an inductive method; he considered physics as a natural object, as a historic-biological process in the life of the species "homo sapiens." The world with his own self appeared to Mach as one continuous mass of sensations, only stronger connected in the "I. " In order to master the multitude of sensations by thinking, Mach considers the principles of "economy" and of adaptation "of thoughts among themselves and to the facts"; so he is driven toward sensualism and empiricism, still avoiding any dogmatic system and continually asking the deeper questions of the validity of the underlying principles of the physical sciences, a problem of philosophy which he is unable to solve.

Dingler devotes a special chapter to Mach's relation to relativity. Mach considered all motions as relative, even the rotations; he rejected absolute space and time. Rotations are relative with respect to the stars. This thought plays an important rôle in the general theory of relativity by A. Einstein, a theory which Mach decidedly refused to accept.

Mach's principal work is probably *Die Mechanik in ihrer Entwicklung*. This classical work forms largely the basis of Dingler's discussion. I should have liked to see a deeper study of Mach's *Die Analyse der Emphindungen*. Even without this analysis I wish to recommend this beautiful little book of Dingler's to the physicists.—Pp. 106. Johann A. Barth, Leipzig, 1924. JAKOB KUNZ

Die Theorien der Radiologie. Marx Handbuch der Radiologie, Vol. 6.—This final volume of the series is devoted largely to theories of electrons and quanta. Chapters on theory of motions of electrons and of passage of alpha and beta particles through matter and a note on the Compton effect are contributed by von Laue. Chapters on the Zeeman effect, experiment and theory, are by Zeeman and Lorentz. A brief statement is given by Sommerfeld and Wentzel of the principles of quantization and their extension to non-hydrogenic atoms. Experiments on excitation of atoms by radiation and by electronic and atomic collisions and the theoretical bearing of the work are compactly presented by Joos. A long chapter by Riecke on electron theories of metals, written in 1913, is supplemented by von Laue. Vegard gives a detailed account of observations and theories of the "Northern Lights." Debye contributes a thorough presentation of theories of electric and magnetic molecular properties.

The names of the contributors vouch for the quality of the papers. In a compilation of this type some overlapping and many omissions are unavoidable. Generally speaking, the omissions (notably in various phases of the quantum theory) are adequately covered in other recently published books, while less accessible material has been given well merited prominence.—Pp. 806. Akademische Verlagsgesellschaft m.b. H. Leipzig, 1924, Price, $10.00 bound; $9.60 unbound. F. L. MOHLER

Grundbegriffe der Mechanischen Technologie der Metalle. GEORGE SACHS.—This book, which is volume II of a series entitled Der Metallische Werkstoff, Gewinnung, Behandlung, Veredlung and edited by W. Guertler, is addressed to the reader with physical training but with no acquaintance with technical operations. It endeavors to present a summary of all the fundamental experimental facts and of the established theory of those mechanical properties of metals which are involved in ordinary engineering and manufacturing operations. A knowledge of a certain amount of the material of this book should be in the possession of every liberally educated physicist, for the behavior of many kinds of physical instrument is affected by such phenomena as elastic hysteresis, for instance. The physicist whose interests take him closer to technology will find this a most valuable summary of a very wide and complicated field, in which there has been much recent progress, and which is nowhere collected into accessible form.

The book is mostly concerned with the behavior of pure metals outside the range in which Hooke's law holds, that is, in the range of permanent set or flow or elastic after-effects, which is really the actual range of all the metals of practice. In the first hundred pages the behavior of metals is described disregarding their small scale crystal structure including the usual subject matter of the testing laboratory, such as tensile, compression and torsion tests, with a discussion of the various hardening effects of over-strain. There follows a longer discussion of the part played by crystal structure in deformation and hardening. This proceeds from an interesting discussion of the recent work of Polany and his collaborators on the deformational properties of single metal crystals, which will be of interest to the pure physicist quite apart from the more technical applications, to a discussion of all the complicated properties of metals which involve their structure as crystalline aggregates. The range of facts covered in this discussion is very wide! The comparatively small space devoted to a discussion of the various theories of the phenomena indicates how far this field is from being a closed one. At the end is a summary in about fifty pages of the mechanical properties of alloys, which will be convenient for those who do not care to consult the more elaborate works. There is also a long bibliography, probably as complete as could be expected in a work of this character, which will be useful to many. The convenience of the book for reference purposes is much increased by a very complete index.—Pp. xii+319, 23×15 cm, with 29 tables and 232 diagrams. Akademische Verlagsgesellshaft M.B.H., Leipzig. 1925. Unbound $3.15, bound in cloth $3.60. P. W. BRIDGMAN

Physikalisches Handwörterbuch. ARNOLD BERLINER and K. SCHEEL.—It is said to be impossible to indict a whole nation, and it must be equally so to review a whole dictionary. However, here are some facts about this distionary; it is over 900 pages long, well printed in double columns on good paper and well bound. The pages are $7\frac{1}{2}'' \times 10\frac{1}{2}''$. The articles range in length from a sentence to several pages, and cover not only the field of physics, but large areas of chemistry, astronomy, geophysics, meteorology, even of geology. The list of authors extends to fifty-nine and includes such impressive names as Freundlich, Gerlach, Grebe, Gumlich, Marx, Pauli, von Rohr, and Westphal. The articles and cross-references are arranged in a single alphabetical series, as in a regular dictionary, not in a series of articles with an index to provide the cross-references, as in an encyclopædia.

As for the quality of the articles, they are much better than I should have thought possible. It does not seem promising to find the information about the contemporary atom-model distributed under the scattered headings *Bohrsches Korrespondenzprinzip, Bohr-Rutherfordsches Atom, Quantenzahlen, Quantentheorie, Adiabatenhypothese, Zeemaneffekt, Storungstheorie*, and I do not know how many others; but this system has the great advantage that one can understand the account of a subject printed, say, on page 500, without being forced to read all through from page 1 to page 499 as a preliminary. Some of the authors have not hesitated to give condensed synopses of such subjects as canonical equations, theory of perturbations, metallic reflection, and equations of impact. The articles on the various aspects of atomic theory seem to represent the state of knowledge "as of" about 1922; the book is dated 1924, but the difference between these dates is easy to justify, and is explained in the unusually candid preface. The most inadequate article I have noticed is that on photo-electricity (masked as *Hallwachseffekt*) which might have been written in 1912. Curiously enough, there is no article headed *Elektron* —only a poor cross-reference appears under this head—but *Subelektron* has a paragraph. However, I do not wish to end on a note of dispraise. The dictionary is distinctly recommendable for libraries, although the individual physicist may well hesitate to pay the price (which, however, seems not exorbitant as prices go).—Pp. vi+903. Julius Springer, Berlin. 1924. Price $9.30.

KARL K. DARROW

College Physics. A. WILMER DUFF.—This book is intended as a textbook for a beginning course, of which demonstration lectures form a part The book is therefore concise, and does not contain a great deal of purely illustrative material or technical applications. The topics treated in the book are clearly presented and the phenomena described are intimately connected with the principles to be illustrated.

Reversing the usual order, statics is presented before dynamics. Unity in the treatment of the subject matter is sought by using energy as the fundamental idea throughout. To this end the introduction of the ideas of work and energy is made in the very beginning, and they are used in the subject of statics, as well as in the later topics. A novel frontispiece emphasizes the important rôle of energy as the fundamental thing in physics. It presents "A Brief History of Physics" in the form of a branching tree and should prove instructive.

Many teachers will feel the lack of a discussion on the subject of dimensions. The substitution of the names "Harmonic Vibration" and "Harmonic Oscillation" for Simple Harmonic Motion and Angular Simple Harmonic Motion seems rather unfortunate as long as the latter terms are used almost universally in the literature of physics.

There are discussions, in the appropriate places in the book, of some of the results of modern research. These discussions are not intended to give the student a working knowledge of the topics treated, but they do serve to give him some idea of the trend in modern physics. References are given for more extended reading. Among the modern topics treated are, Relativity, Electron Theory, Atomic Structure, Quantum Theory, Bohr's Theory of Spectra, and Crystal Structure. Many teachers will wish for a more complete incorporation of the electron theory into the treatment of electricity.

Among the features which should prove of value to students are the "Suggestions to Students" in the beginning of the book, the lists of suggestive questions and the numerical problems at the end of the chapters, and the many worked-out problems. In an appendix are given calculus derivations of some important formulas. This book should prove a valuable addition to the available textbooks.—Pp. xii+484, 499 figures, 27 tables. Longmans, Green and Co.; New York. 1925. Price $3.80.

J. R. COLLINS

Physics for Technical Students. WILLIAM BALLANTYNE ANDERSON.—Second edition, revised and enlarged.—From the preface, this edition contains 50 new figures

and over 200 new problems. A new chapter in "Recent Researches and Theories" and a few topics and tables have been added, but the general arrangement and scope is unchanged. "Every paragraph has been carefully examined to see if it could be improved," so that the revision has been thorough.

As the textbook is intended mainly for students of agriculture and engineering, the practical applications have been emphasized as is shown in the treatment of the telephone and telegraph, and in chapters on Meteorology, Steam and Gas Engines, Musical Instruments, Optical Instruments, Electrical Measuring Instruments, Dynamo-electric Machines, Electromagnetic Waves and Radiotelegraphy. Recent advances including Discharge of Electricity through Gases and Radioactivity are also presented. Nevertheless, the fundamental theory is presented very fully.

It seems impracticable to get away from the dogmatic method. Thus, we find forces used in statics before the measurement of forces is discussed and then force defined as *ma* before a discussion of the Atwood machine or a statement of Newton's Laws. While for most students such a treatment may not be annoying or confusing, it would not seem to foster a critical scientific attitude nor cultivate intellectual self-reliance. The figures, though not as numerous as in some texts, are well drawn and seem well chosen. On the whole, the book seems well balanced and should serve well as a basis for a thorough course for technical and other serious students.—Pp. xxiii+827, 373 figures, over 600 problems. McGraw-Hill. $4.00. 1925. G.S.F.

Mélanges de Mathematiques et de Physiques. ÉMILE PICARD.—In this volume the permanent secretary of the Academy of Sciences of Paris has gathered together a number of the papers and addresses of Picard on a variety of subjects. Many of the papers deal with the lives and works of celebrated mathematicians, notably Halphen, Weierstrass, Sylvester, Hermite, and Abel. The paper on the solution of the telegraphic equation in the form of an integral equation is included and also a short note on the problem of a disk free to rotate about an axis, the disk carrying a particle moving in a closed curve.

The volume is of interest in showing the breadth of view of the author, a trait which is becoming too rare in these days of specialized effort.—Pp. 364. Paris, Gauthiers-Villars. 25 fr. E. P. ADAMS